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Continued on the inside back cover

Hydrothermal phase equilibria in $\text{Er}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ and $\text{Tm}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ systems

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Abstract. Isobaric phase equilibria in $\text{Er}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ and $\text{Tm}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ systems have been determined at 650 and 1300 bars and temperature range of 100–800°C. The equilibria depend on the mole fraction of CO_2 in the coexisting fluid. The stable phases: $\text{Ln}(\text{OH})_3$, $\text{Ln}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Ln}(\text{OH})\text{CO}_3$ —orthorhombic, $\text{Ln}_2\text{O}_2\text{CO}_3$ —hexagonal, LnOOH and Ln_2O_3 —cubic are common to both the systems. Additional phases observed in the thulium system are $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$. Two other phases isolated are $\text{Tm}_6\text{O}_2(\text{OH})_8(\text{CO}_3)_3$ and $\text{Tm}_4(\text{OH})_6(\text{CO}_3)_3$ which are stabilised only in the presence of alkali impurities. Stability field of $\text{Ln}(\text{OH})_3$ is limited to $X_{\text{CO}_2} < 0.01$. $\text{Tm}(\text{OH})\text{CO}_3$ does not stabilise at low X_{CO_2} ; therefore TmOOH coexists with all the phases other than $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$. When $X_{\text{CO}_2} = 1$, the stable phases are $\text{Tm}_2\text{O}_2\text{CO}_3$ and Tm_2O_3 in the order of increasing temperature. The normal carbonate, $\text{Tm}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ has no stability at higher pressures.

Keywords. Hydrothermal equilibria; lanthanide carbonates; basic carbonates; thulium.

1. Introduction

Ternary heterogeneous systems: $\text{Ln}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ (Ln = Lanthanides), under hydrothermal conditions are important for mineral syntheses and crystal growth of carbonates, hydroxides and oxides of lanthanides. Solid phases isolated from high pressure experiments (Christensen 1970; Chai and Mroczkowski 1978) as well as experiments at low temperature and one atmosphere pressure (Dexpert *et al* 1972; Sawyer *et al* 1973; Caro and Lemaitre-Blaise 1970) were isostructural with minerals like lanthanite, tengerite (Tareen *et al* 1980a) bastnaesite and ancylite. The present authors have investigated systematically the phase diagrams in different $\text{Ln}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ systems. Phase diagrams for the lanthanides of the ceric group have been reported earlier (Kutty *et al* 1978; Tareen and Kutty 1980). Extending this work to heavier lanthanides, we have found that there are new phases stabilised under pressure. Marked differences are observed in $\text{Tm}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ system, when compared to the corresponding Er_2O_3 system.

2. Experimental

Er_2O_3 (Leico Industries, New York) and Tm_2O_3 (Koch-light Labs, U.K) were of 99.99% purity. Details of experiments for hydrothermal equilibria studies and

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maintenance of known partial pressures of CO_2 and H_2O are as reported earlier (Kutty *et al* 1978; Viswanathiah *et al* 1978). Methods of chemical analyses were reported by Tareen and Kutty (1980). X-ray powder patterns were taken with Philips PW 1041 diffractometer. IR spectra were recorded on Perkin Elmer 597 spectrometer or Carl-Zeiss Jena UR 10 in the range of $400\text{--}4000\text{ cm}^{-1}$ both in KBr and Nujol mull.

3. Results and discussion

Isobaric (650 bars) phase diagram of $\text{Er}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ (figure 1) showed six stable phases: $\text{Er}(\text{OH})_3$, $\text{Er}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Er}(\text{OH})\text{CO}_3$ —orthorhombic, $\text{Er}_2\text{O}_2\text{CO}_3$ —hexagonal, ErOOH —monoclinic and Er_2O_3 —cubic. Isobaric phase diagrams at 1300 bars exhibited the same set of stable phases, except that the area of hydroxides— $\text{Er}(\text{OH})_3$ and ErOOH —shift to slightly lower X_{CO_2} (mole fraction of CO_2) values. There are six triple-points; which are invariant points at constant P-T values; temperature-wise the lowest one is around 130°C involving $\text{Er}(\text{OH})_3$, $\text{Er}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{Er}(\text{OH})\text{CO}_3$; the highest temperature triple-point is that of ErOOH — $\text{Er}_2\text{O}_2\text{CO}_3$ — Er_2O_3 . Compared to the phase diagram of $\text{Gd}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ (Tareen and Kutty 1980), the field of trihydroxide is broader, extending up to $X_{\text{CO}_2} = 0.05$. For the lighter lanthanides, stability of $\text{Ln}(\text{OH})_3$ is very limited ($X_{\text{CO}_2} = 0.008$ for Nd; $X_{\text{CO}_2} = 0.003$ for Gd). Around 260°C , $\text{Er}(\text{OH})_3$ converts to ErOOH and further to Er_2O_3 —cubic at 655°C , when X_{CO_2} approaches zero. At higher values, $\text{Er}(\text{OH})_3$ transforms to $\text{Er}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ which is isostructural with the mineral tengerite. The crystalline phase equivalent to lanthanite, $\text{Ln}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, is not stabilised under hydrothermal conditions. With

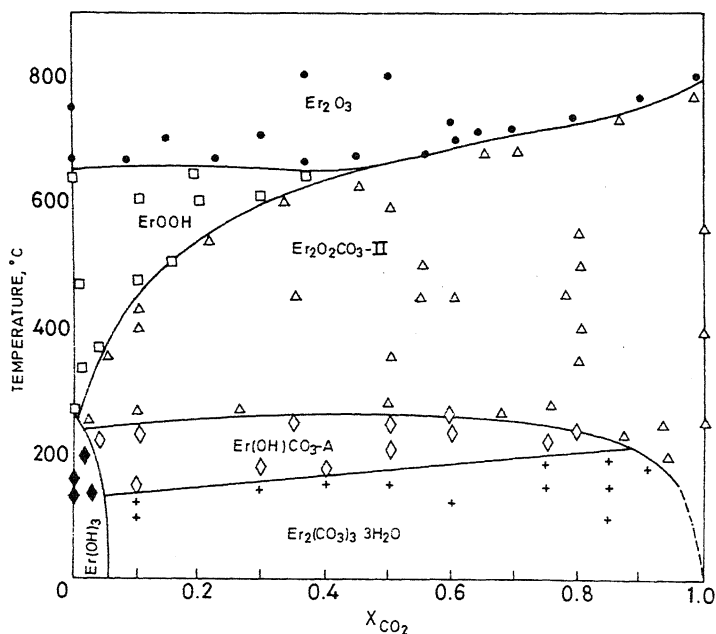


Figure 1. $T\text{--}X_{\text{CO}_2}$ phase diagram for $\text{Er}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ system at 650 bars.

rise in temperature, $\text{Er}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ directly converts to $\text{Er}(\text{OH})\text{CO}_3$ with orthorhombic symmetry (isostructural with the mineral ancylite). There is no hydrothermal stability for $\text{Er}(\text{OH})\text{CO}_3$ —hexagonal, which is the prevalent phase in lanthanides lighter than Gd. In Nd_2O_3 — H_2O — CO_2 system, the stable $\text{Nd}(\text{OH})\text{CO}_3$ phase, is equivalent to bastnaesite while for Gd, both hexagonal and orthorhombic phases of $\text{Gd}(\text{OH})\text{CO}_3$ are stable. There is X_{CO_2} -dependent phase transformation at 1500 bars, in $\text{Gd}(\text{OH})\text{CO}_3$. In figure 1, $\text{Er}_2\text{O}_2\text{CO}_3$ —hexagonal, with a broader field of stability, is stable at higher temperatures. With increasing X_{CO_2} it transforms to Er_2O_3 .

Figures 2A–C gives the isothermal sections of the three-component system at 650 bars, showing the compositional stability of the various phases at 150°, 550° and 700°C respectively. The section at 150°C (figure 2A) shows that $\text{Er}(\text{OH})_3$, $\text{Er}(\text{OH})\text{CO}_3$ and $\text{Er}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ become stable, as X_{CO_2} value increases. $\text{Er}_2\text{O}_2\text{CO}_3$ phase is stable at $X_{\text{CO}_2} = 1$ i.e. in the system nearly free of H_2O . The section at 550°C (figure 2B) has only two stable phases, ErOOH and $\text{Er}_2\text{O}_2\text{CO}_3$ in the increasing order of X_{CO_2} . The section at 700°C shows that Er_2O_3 and $\text{Er}_2\text{O}_2\text{CO}_3$ are the only persistent phases in equilibrium with the H_2O -free fluid.

Based on 72 experimental equilibrium points, T- X_{CO_2} diagram for Tm_2O_3 — H_2O — CO_2 system has been constructed (figure 3). This diagram is different from those of the previously reported Ln_2O_3 — H_2O — CO_2 system including that of Er_2O_3 . $\text{Tm}(\text{OH})\text{CO}_3$ disappears at higher X_{CO_2} and at higher temperature, giving way

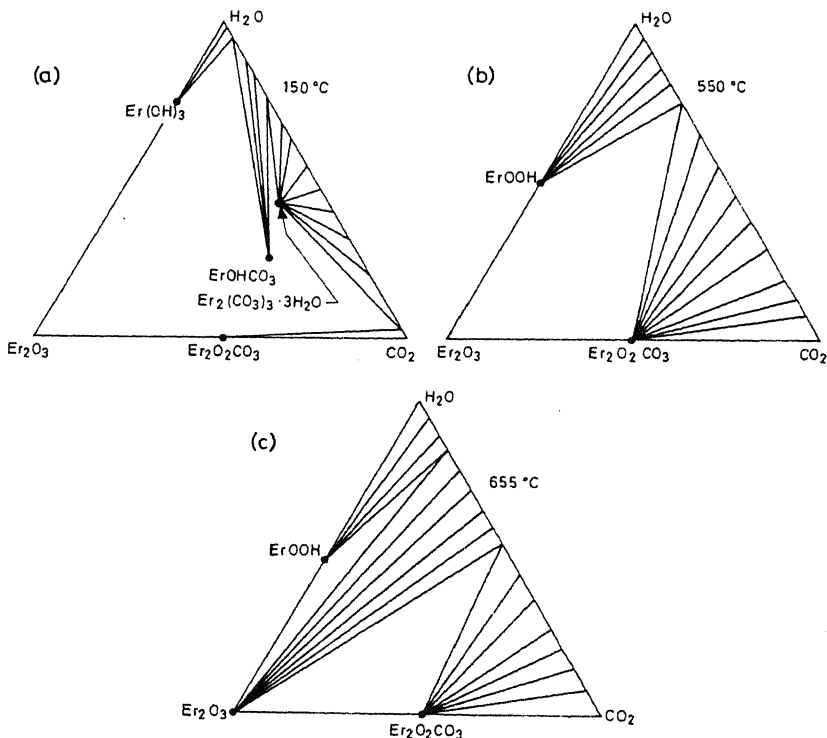


Figure 2. Isothermal sections at a. 150°C. b. 550°C and c. 700°C for Er_2O_3 — H_2O — CO_2 at 650 bars.

to hitherto unreported hydroxy carbonates. Besides, $\text{Tm}(\text{OH})\text{CO}_3$ is not stable at very low concentration of CO_2 ($X_{\text{CO}_2} \sim 0.01$) and converts to TmOOH . The new carbonate phases with definite reproducibility are $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$, and $\text{TmO}(\text{OH})_2\text{CO}_3$. The phase boundaries between $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$, $\text{Tm}(\text{OH})\text{CO}_3$ and $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ are very sensitive to small variations in X_{CO_2} values and minor temperature fluctuations. The reason will be evident when the isothermal sections are considered. The boundaries are tentatively demarcated with dashed lines (figure 3) though the diagram is constructed from data points of highest reproducibility. Within the boundary of $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and $\text{Tm}(\text{OH})\text{CO}_3$, two more phases could be isolated $\text{Tm}_6\text{O}_2(\text{OH})_8(\text{CO}_3)_3$ and $\text{Tm}_4(\text{OH})_6(\text{CO}_3)_3$. These phases could only sparingly be reproduced and depend on alkali contamination in ppm concentrations. Since these phases may not be stable in highly pure $\text{Tm}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ system, they are not plotted in figure 3. The other stable phases *viz* $\text{Tm}(\text{OH})_3$, TmOOH , $\text{Tm}_2\text{O}_2\text{CO}_3$ —hexagonal and Tm_2O_3 —cubic are identical to those of Er_2O_3 system. The complexity in the nature of stable carbonates is only in the region between $\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tm}_2\text{O}_2\text{CO}_3$. Another new feature in figure 3 is the coexistence of TmOOH with $\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Tm}(\text{OH})\text{CO}_3$, $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and $\text{Tm}_2\text{O}_2\text{CO}_3$ whereas in Er_2O_3 system, ErOOH converts only to $\text{Er}_2\text{O}_2\text{CO}_3$ with increased X_{CO_2} .

Figures 4A–C show the isothermal sections of $\text{Tm}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ at 650 bars. At 150°C , $\text{Tm}(\text{OH})_3$, $\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Tm}(\text{OH})\text{CO}_3$, and $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$ are the stable phases. At this temperature, $\text{Tm}_2\text{O}_2\text{CO}_3$ is barely stable in the H_2O -free system. At 350°C , these phases are replaced by TmOOH , $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and $\text{Tm}_2\text{O}_2\text{CO}_3$ (figure 4B). At 625°C , $\text{Tm}_2\text{O}_2\text{CO}_3$ and Tm_2O_3 are the only stable phases (figure 4C). It is evident from figure 4A, B that the isothermal stability fields of $\text{Tm}(\text{OH})\text{CO}_3$, $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and $\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ are very narrow such that slight

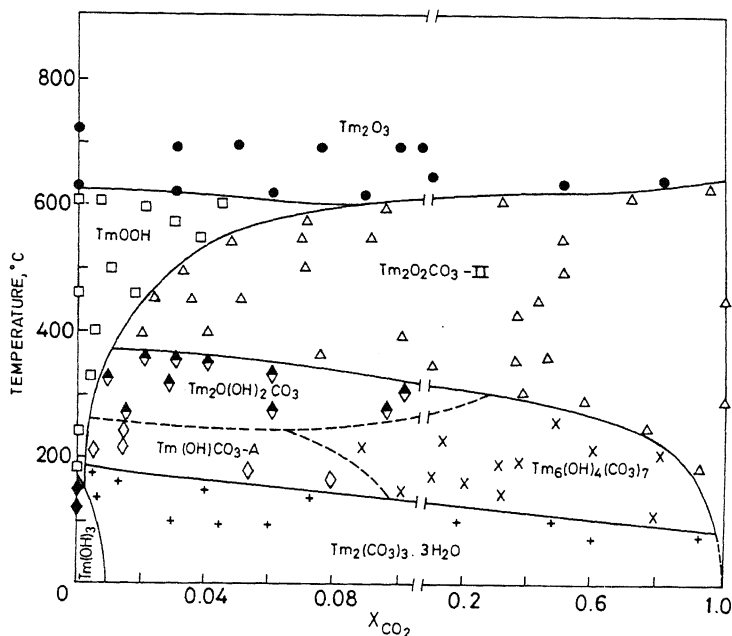


Figure 3. $T\text{--}X_{\text{CO}_2}$ phase diagram for $\text{Tm}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ system at 650 bars.

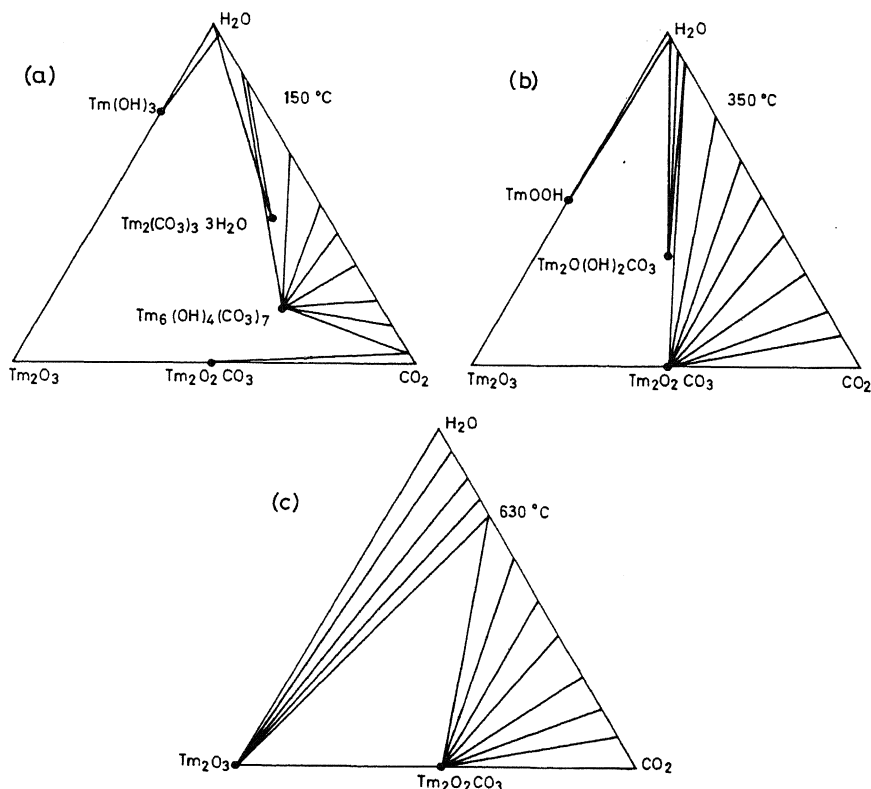


Figure 4. Isothermal sections at a. 150°C, b. 350°C and c. 630°C for $\text{Tm}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ at 650 bars.

compositional difference in the starting materials will alter the coexisting solid phases. The tie-lines between $\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Tm}(\text{OH})\text{CO}_3$, $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$ overlap considerably. Hence the demarcation of boundaries between these phases in figure 3 is difficult.

Following are the chemical equilibria involved in $\text{Tm}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ system:

- (i) $2 \text{Tm}(\text{OH})_3 + 3\text{CO}_2 = \text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$
- (ii) $\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O} = 2 \text{Tm}(\text{OH})\text{CO}_3 + 2\text{H}_2\text{O} + \text{CO}_2$,
- (iii) $2 \text{Tm}(\text{OH})\text{CO}_3 = \text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3 + \text{CO}_2$,
- (iv) $\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O} = \text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O}$,
- (v) $3 \text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3 + 4 \text{CO}_2 + 0.5 \text{H}_2\text{O} = \text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$,
- (vi) $\text{Tm}(\text{OH})_3 = \text{TmOOH} + \text{H}_2\text{O}$,
- (vii) $\text{TmOOH} + \text{CO}_2 = \text{Tm}(\text{OH})\text{CO}_3$,
- (viii) $2 \text{TmOOH} + \text{CO}_2 = \text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$,
- (ix) $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3 = \text{Tm}_2\text{O}_2\text{CO}_3 + \text{H}_2\text{O}$,
- (x) $2 \text{TmOOH} + \text{CO}_2 = \text{Tm}_2\text{O}_2\text{CO}_3 + \text{H}_2\text{O}$,
- (xi) $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7 = 3 \text{Tm}_2\text{O}_2\text{CO}_3 + 4\text{CO}_2 + 2\text{H}_2\text{O}$,
- (xii) $2 \text{TmOOH} = \text{Tm}_2\text{O}_3 + \text{H}_2\text{O}$,
- (xiii) $\text{Tm}_2\text{O}_2\text{CO}_3 = \text{Tm}_2\text{O}_3 + \text{CO}_2$.

3.1 Characterisation of carbonate phases

Table 1 gives the chemical composition of stable phases isolated from hydrothermal experiments. The agreement between Ln_2O_3 , H_2O and CO_2 contents observed and calculated according to the formula given in the last column is reasonable in all the cases. The phase purity of analysed samples is confirmed by both x-ray powder pattern and IR absorption spectrum.

The unit cell constants derived from x-ray powder diffraction data for the phases identical to those from Gd_2O_3 system are listed in table 2. The indexed powder data for $\text{Ln}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Ln}(\text{OH})_3$, LnOOH , $\text{Ln}_2\text{O}_2\text{CO}_3$ (hexagonal), $\text{Ln}(\text{OH})\text{CO}_3$ (orthorhombic) and Ln_2O_3 (cubic) are reported earlier for many of the lanthanides (Sawyer *et al* 1973; Tareen *et al* 1980a,b; Kutty *et al* 1978; Tareen and Kutty 1980; Chai and Mroczkowski 1978). The indexed x-ray data for $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$ are given in table 3 Christensen (1973) and Chai and Mroczkowski (1978) have reported $\text{Y}_2\text{O}(\text{OH})_2\text{CO}_3$ as a stable phase under hydrothermal conditions. The x-ray data for the metastable phases $\text{Tm}_6\text{O}_2(\text{OH})_8(\text{CO}_3)_3$ and $\text{Tm}_4(\text{OH})_6(\text{CO}_3)_3$

Table 1. Chemical analysis of hydrothermally stable phases.

Lanthanide	Ln_2O_3		H_2O		CO_2		Chemical formula
	obsd	calc	obsd	calc	obsd	calc	
Ln = Er	87.7	87.63	12.43	12.37	—	—	$\text{Er}(\text{OH})_3$
	95.4	95.51	4.55	4.49	—	—	ErOOH
	78.15	78.30	3.75	3.69	15.20	18.01	$\text{Er}(\text{OH})\text{CO}_3$
	67.1	67.28	9.60	9.50	23.2	23.22	$\text{Er}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$
	89.72	89.68	—	—	10.30	10.32	$\text{Er}_2\text{O}_2\text{CO}_3$
Ln = Tm	87.7	87.72	12.20	12.28	—	—	$\text{Tm}(\text{OH})_3$
	95.5	95.55	4.42	4.45	—	—	TmOOH
	78.5	78.45	3.63	3.66	17.85	17.89	$\text{Tm}(\text{OH})\text{CO}_3$
	67.41	67.47	9.48	9.44	23.15	23.09	$\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$
	77.1	77.09	2.41	2.40	20.50	20.51	$\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$
	86.0	86.16	4.0	4.02	10.0	9.82	$\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$
	89.81	89.76	—	—	10.20	10.24	$\text{Tm}_2\text{O}_2\text{CO}_3$

Table 2. Unit cell parameters of more common phases.

Phase	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	β	Crystal system
$\text{Er}(\text{OH})_3$	6.250	—	3.551	—	Hexagonal
ErOOH	5.935	3.622	4.505	109.3°	Monoclinic
$\text{Er}(\text{OH})(\text{CO}_3)$	4.963	8.452	7.201	—	Orthorhombic
$\text{Er}_2\text{O}_2\text{CO}_3$	3.821	—	14.984	—	Hexagonal
$\text{Er}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	6.182	9.220	15.423	—	Orthorhombic
$\text{Tm}(\text{OH})_3$	6.230	—	3.501	—	Hexagonal
TmOOH	4.251	3.588	6.014	112.2°	Monoclinic
$\text{Tm}(\text{OH})\text{CO}_3$	4.960	8.449	7.198	—	Orthorhombic
$\text{Tm}_2\text{O}_2\text{CO}_3$	3.781	—	15.165	—	Hexagonal
$\text{Tm}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$	6.180	9.215	15.420	—	Orthorhombic

are also presented in table 3, though no indexing has been attempted. However, their identity as separate phases is substantiated by these data.

IR adsorption spectra of all the stable phases have been recorded. Only the spectra of $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$, $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and those of the metastable phases are presented in figure 5. The number of absorption bands indicates that the CO_3^{2-} ions have the site symmetry of C_s or C_{2v} in all the cases; hence the notations of Gatehouse *et al* (1958) are followed in figure 5. CO_3^{2-} ion may be coordinated to the metal ion in more than one way, giving rise to unidentate or bidentate complexes. Fujita *et al* (1962) have shown that the extent of splitting ($\nu_3-\nu_1$) can be taken as an approximate index where the unidentate carbonate ($\sim 100\text{cm}^{-1}$) has lower splitting than bidentate ion ($\sim 300\text{cm}^{-1}$). Complication arises from the fact that there are more absorption bands than can be expected from the six theoretical fundamentals of CO_3^{2-} ion with C_s or C_{2v} symmetry. Caro *et al* (1972) have suggested that there may be more than one kind of site in the crystal structure for carbonate ions. This would multiply the corresponding

Table 3. X-ray powder diffraction data for the newer phases from $\text{Tm}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ system.

$\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$			$\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$			$\text{Tm}_6\text{O}_2(\text{OH})_8(\text{CO}_3)_3$		$\text{Tm}_4(\text{OH})_6(\text{CO}_3)_3$	
<i>d</i> (Å)	<i>I</i>	<i>hkl</i>	<i>d</i> (Å)	<i>I</i>	<i>hkl</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
6.003	w	010	6.2115	vvs	100	12.10	29	9.92	20
4.701	vvs	002	4.288	ms	110	4.982	28	9.02	98
3.874	ms	110	3.200	s	014	4.268	29	6.071	100
4.694	vw	012	2.987	ms	020	4.009	43	5.212	37
3.913	mw	—	2.751	s	210	3.913	40	5.037	13
2.987	s	020	2.696	w	015	3.022	100	4.982	15
2.885	mw	—	2.571	w	204	2.618	43	4.772	10
2.526	ms	022	2.363	m	214	1.852	36	4.646	95
2.476	m	201	2.257	ms	124	1.583	21	4.538	6
2.349	s	004	2.150	ms	220			4.228	20
2.262	vw	122	1.951	s	224			4.101	17
2.102	mv	212	1.920	w	304			4.018	13
2.011	mw	—	1.585	w	133			3.930	20
1.941	m	220	1.764	vw	034			3.769	20
1.850	s	130	1.722	ms	108			3.722	22
1.830	ms	032	1.675	w	231			3.655	11
1.794	s	015	1.650	vw	231			3.583	10
1.706	m	300	1.616	w	028			3.415	11
1.678	m	301	1.599	w	128			3.336	6
1.562	vw	230						3.268	39
1.497	mw	040	$a = 6.195 \text{ \AA}$					3.213	9
1.428	mw	206	$b = 5.974 \text{ \AA}$					3.108	54
1.276	m	400	$c = 15.158$					3.037	9
1.249	vw	332	$\beta = 97.5^\circ$					3.018	10
$a = 5.118 \text{ \AA}$			Monoclinic					2.968	9
$b = 5.989 \text{ \AA}$								2.871	11
$c = 9.398 \text{ \AA}$								2.839	10
Orthorhombic								and 16 other lines	

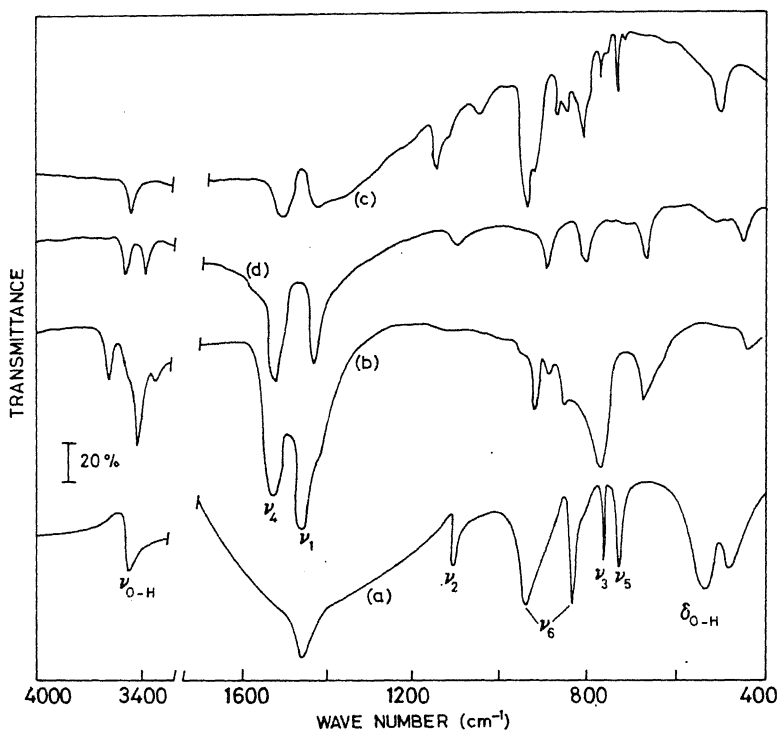


Figure 5. IR spectra of a. $\text{Tm}_6(\text{OH})_4(\text{CO}_3)$, b. $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ c. $\text{Tm}_4(\text{OH})_6(\text{CO}_3)_3$ and d. $\text{Tm}_6\text{O}_2(\text{OH})_8(\text{CO}_3)_3$.

number of fundamentals. A combination of fundamental vibrational modes with lattice modes may give additional bands. Splitting of nondegenerate out-of-plane deformation (ν_6) is a definite evidence for the non-equivalent orientation of CO_3^{2-} ion. The stretching (around 3600 cm^{-1}) and librational modes (around 550 cm^{-1}) for the $(\text{OH})^{-1}$ groups can be noticed in figure 5.

4. Conclusions

There is increased complexity in $\text{Ln}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ phase diagrams of the heavier lanthanides. Additional phases stabilised in Tm_2O_3 system are $\text{Tm}_2\text{O}(\text{OH})_2\text{CO}_3$ and $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$. Other stable phases common to Er and Tm are $\text{Ln}(\text{OH})_3$, $\text{Ln}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, LnOOH , $\text{Ln}(\text{OH})\text{CO}_3$ (orthorhombic) and Ln_2O_3 . In the presence of minor impurities like alkali ions, $\text{Tm}_6\text{O}_2(\text{OH})_8\text{CO}_3$ and $\text{Tm}_4(\text{OH})_6(\text{CO}_3)_3$ are metastably formed. The general hydrothermal behaviour of $\text{Ln}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ system indicates marked differences in the chemical equilibria of heavier lanthanides when compared to those prevailing in lighter lanthanides.

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Ion-solvent interactions of some silver salts in N,N-dimethyl formamide-water mixtures at 30°C

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Abstract. The solvation behaviour of the salts, silver bromate, silver acetate and silver sulphate has been investigated in the binary mixtures of N,N-dimethyl formamide (DMF) and water. The Gibbs energies of transfer of these salts from water to water-DMF mixtures have been calculated from the solubilities of the salts in these mixtures. The transfer free energies of the salts were split into their ionic contributions by using the transfer-free energy of the silver ion in these mixtures obtained on the basis of negligible liquid junction potential (nLJP) method from independent EMF measurements. The solvent transference number, Δ of DMF, was determined by EMF measurements using a suitable galvanic cell with transference. The results have been interpreted in terms of a heteroselective solvation of the salts with the silver ion selectively solvated by DMF and the anions by water.

Keywords. Selective solvation; water-dimethyl formamide mixtures; solubility; EMF method; silver bromate; silver acetate; silver sulphate.

1. Introduction

The determination of solvent transport number, Δ is an important approach to obtain information (Schneider 1976) on the composition of solvation shells of ions in mixed solvents. Δ is defined as the change in the number of moles of one solvent component in the cathode compartment relative to the mean molar velocity of the solvent mixture as reference when one Faraday of electricity is passed through a cell during electrolysis. Δ will be small (usually < 1) for homoselectively solvated electrolytes whereas it will be large (usually > 1) for heteroselectively solvated electrolytes. Further its sign will also indicate the solvent component that preferentially solvates the ions.

Despite the fact that selective solvation of ions in some binary amphiprotic dipolar aprotic solvent mixtures has been studied (Subramanian *et al* 1981; Giridhar and Kalidas 1982), very few results have been reported (Stroka and Schneider 1980; Giridhar and Kalidas 1983) dealing with N,N-dimethyl formamide (DMF) as one of the dipolar aprotic components. Both DMF and water are associated liquids and their heat of mixing is exothermic indicating strong inter component interactions. Although no data on excess thermodynamic quantities such as Gibbs energy or entropy of mixing are available, hydrogen bonded complexes (Singh *et al* 1977) between DMF and water molecules of the type $\text{DMF} \cdot n\text{H}_2\text{O}$ where $n = 2$ to 4 have been suggested. Despite such strong solvent-solvent interactions, DMF-water mixtures conform to Raoult's law at temperatures around 90°C (Ivanova and Geller 1961) and presumably this behaviour is also valid at lower temperatures. The present paper reports the effect of such solvent

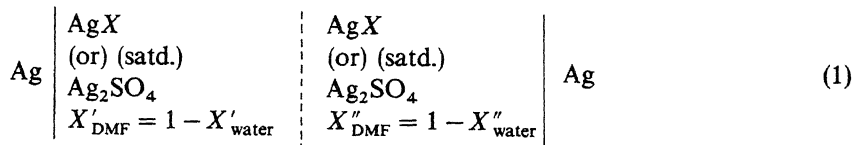
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mixtures having strong interactions among themselves on ion solvation *vis a vis* the solvent mixtures possessing weak interactions among the components. The results of the solvation behaviour of some silver salts such as silver sulphate, bromate and acetate in DMF-water mixtures at 30°C by solvent transport number measurements and by determination of Gibbs energies of transfer of the ions in these mixtures are reported.

2. Experimental

DMF (BDH, LR) after a preliminary distillation under vacuum was dried over anhydrous copper sulphate for a week and distilled under vacuum following the procedure of Faulkner and Bard (1968). It has a boiling point of 45°C at 15 mm Hg pressure, $d^{25} = 0.9441 \text{ g cm}^{-3}$, $n_D^{25} = 1.4269$, sp. conductivity = $1.05 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ in agreement with literature values (Geller 1961).

Doubly-distilled conductivity water was used in the preparation of solvent mixtures. Silver acetate and silver sulphate (S. Merck, Baroda) were dried over P_2O_5 under vacuum before use. Their purity was checked by estimation of their silver content by potentiometry. Silver bromate prepared as described earlier (Janardhanan and Kalidas 1980) was used. The solubility of the salts in various compositions of solvent mixtures was determined potentiometrically as described previously (Kalidas and Sivaprasad 1979). The solvent transport number, Δ has been determined by employing a galvanic cell with transference according to the method of Wagner (1966).



(where $X = \text{BrO}_3$ (or) OAc) and EMF measurements on cell (1) were carried out with a solid state electrometer (Keithley Model 602) over the complete range of water-DMF mixtures keeping the molefraction difference, $(X''_{\text{DMF}} - X'_{\text{DMF}})$ constant throughout. The silver electrodes required for EMF measurements were always prepared afresh according to Carmody (1928). All measurements were carried out at $30 \pm 0.1^\circ\text{C}$.

3. Results and discussion

The Gibbs transfer energy of the salt (from water to its mixtures with DMF) can be calculated from the solubility data by using the relation

$$\Delta G_t^0(\text{salt}) = -2.303 RT \log \frac{K_{SP}(\text{solvent})}{K_{SP}(\text{water})}, \quad (1)$$

and the results are given in tables 1-3. The solubilities of silver bromate and silver acetate are related to the respective thermodynamic solubility products by

$$K_{SP} = S^2 \gamma_{\pm}^2, \quad (2)$$

and for silver sulphate,

$$K_{SP} = 4S^3 \gamma_{\pm}^3, \quad (3)$$

Table 1. Solubility of silver (I) bromate and Gibbs transfer free energies of AgBrO_3 , Ag^+ and BrO_3^- from water to water-DMF mixtures at 30°C (molal scale).*

Mole fraction of DMF (X_{DMF})	Solubility of $\text{AgBrO}_3 \times 10^3$ (mol kg ⁻¹)	$\Delta G_i^0(\text{AgBrO}_3)$ (kJ mol ⁻¹)	$\Delta G_i^0(\text{Ag}^+)$ (kJ mol ⁻¹)	$\Delta G_i^0(\text{BrO}_3^-)$ (kJ mol ⁻¹)
0	10.2	0	0	0
0.1	5.26	3.2 ± 0.02	-2.3 ± 0.01 (-3.5)	5.5 ± 0.03
0.2	3.68	5.1 ± 0.05	-4.4 ± 0.01 (-8.6)	9.5 ± 0.06
0.3	2.19	7.7 ± 0.04	-6.2 ± 0.01 (-12.6)	13.9 ± 0.05
0.4	1.83	8.6 ± 0.04	-7.8 ± 0.01 (-14.4)	16.4 ± 0.05
0.5	1.31	10.2 ± 0.04	-9.1 ± 0.01 (-15.4)	19.3 ± 0.05
0.6	0.90	12.1 ± 0.01	-10.2 ± 0.01 (-16.4)	22.3 ± 0.02
0.7	0.62	14.0 ± 0.01	-11.1 ± 0.01 (-17.4)	25.1 ± 0.02
0.8	0.52	14.9 ± 0.01	-11.6 ± 0.01 (-18.6)	26.5 ± 0.02
0.9	0.34	17.0 ± 0.01	-12.1 ± 0.01 (-19.6)	29.1 ± 0.02
1.0	0.21	19.5 ± 0.01	-11.7 ± 0.01 (-20.6)	31.2 ± 0.02

* The values in parenthesis in tables 1-3 correspond to the one determined on the basis of reference electrolyte method by Kundu and Parker (1981).

Table 2. Solubility of silver(I) acetate and Gibbs transfer free energies of AgOAc , Ag^+ and OAc^- from water to water-DMF mixtures at 30°C (molal scale).*

Molefraction of DMF (X_{DMF})	Solubility of $\text{AgOAc} \times 10^3$ (mol kg ⁻¹)	$\Delta G_i^0(\text{AgOAc})$ (kJ mol ⁻¹)	$\Delta G_i^0(\text{Ag}^+)$ (kJ mol ⁻¹)	$\Delta G_i^0(\text{OAc}^-)$ (kJ mol ⁻¹)
0	72.0	0	0	0
0.1	29.4	4.3 ± 0.01	-2.3 ± 0.01 (-3.5)	6.6 ± 0.02
0.2	12.5	8.5 ± 0.01	-4.4 ± 0.01 (-8.6)	12.9 ± 0.02
0.3	5.88	12.1 ± 0.03	-6.2 ± 0.01 (-12.6)	18.3 ± 0.04
0.4	3.05	15.4 ± 0.01	-7.8 ± 0.01 (-14.4)	23.2 ± 0.02
0.5	1.58	18.7 ± 0.01	-9.1 ± 0.01 (-15.4)	27.8 ± 0.02
0.6	1.44	19.2 ± 0.02	-10.2 ± 0.01 (-16.4)	29.4 ± 0.03
0.7	1.32	19.6 ± 0.03	-11.1 ± 0.01 (-17.4)	30.7 ± 0.04
0.8	0.72	22.6 ± 0.01	-11.6 ± 0.01 (-18.6)	34.2 ± 0.02
0.9	0.48	24.6 ± 0.05	-12.1 ± 0.01 (-19.6)	36.7 ± 0.06
1.0	0.62	23.4 ± 0.01	-11.7 ± 0.01 (-20.6)	35.1 ± 0.02

*

where $\gamma_{\pm}$ is the mean molal activity coefficient of the electrolyte under consideration calculated from the extended Debye-Hückel equation with $a = 6.5 \text{ \AA}$ for silver bromate and silver sulphate and $a = 7 \text{ \AA}$ for silver acetate. The Gibbs transfer energy of silver ion from water to water-DMF mixtures was determined on the basis of negligible liquid junction potential method proposed by Alexander *et al* (1972). The same quantity reported (Kundu and Parker 1981) on the basis of reference electrolyte method at 25°C is also given in tables 1-3 for comparison. The transfer-free energy of

Table 3. Solubility of silver(I) sulphate and Gibbs transfer free energies of Ag_2SO_4 , and SO_4^{2-} from water to water-DMF mixtures at 30°C (molal scale).*

Molefraction of DMF (X_{DMF})	Solubility of $\text{Ag}_2\text{SO}_4 \times 10^3$ (mol kg ⁻¹)	$\Delta G_i^0(\text{Ag}_2\text{SO}_4)$ (kJ mol ⁻¹)	$\Delta G_i^0(\text{Ag}^+)$ (kJ mol ⁻¹)	$\Delta G_i^0(\text{SO}_4^{2-})$ (kJ mol ⁻¹)
0	29.3	0	0	0
0.1	6.4	11.0 ± 0.02	-2.3 ± 0.01 (-3.5)	15.6 ± 0.0
0.2	1.4	22.3 ± 0.02	-4.4 ± 0.01 (-8.6)	31.1 ± 0.0
0.3	0.64	28.1 ± 0.02	-6.2 ± 0.01 (-12.6)	40.5 ± 0.0
0.4	0.19	37.2 ± 0.02	-7.8 ± 0.01 (-14.4)	52.8 ± 0.0
0.5	0.13	40.1 ± 0.08	-9.1 ± 0.01 (-15.4)	58.3 ± 0.1
0.6	0.08	43.6 ± 0.02	-10.2 ± 0.01 (-16.4)	64.0 ± 0.0
0.7	0.06	45.7 ± 0.02	-11.1 ± 0.01 (-17.4)	67.9 ± 0.0
0.8	0.053	46.8 ± 0.02	-11.6 ± 0.01 (-18.6)	70.0 ± 0.0
0.9	0.048	47.5 ± 0.02	-12.1 ± 0.01 (-19.6)	71.7 ± 0.0
1.0	0.041	48.7 ± 0.02	-11.7 ± 0.01 (-20.6)	72.1 ± 0.0

the salt is related to the transfer energies of the corresponding ions by

$$\Delta G_i^0(\text{Ag}X) = \Delta G_i^0(\text{Ag}^+) + \Delta G_i^0(X^-),$$

where $X^- = \text{BrO}_3^-$ and OAc^- in the case of silver bromate and acetate and for silver sulphate, it is given by

$$\Delta G_i^0(\text{Ag}_2\text{SO}_4) = 2\Delta G_i^0(\text{Ag}^+) + \Delta G_i^0(\text{SO}_4^{2-}).$$

It is seen (tables 1-3) that the solubility of all the three salts decreases continuously with the addition of DMF excepting for silver acetate where there is a slight rise in p DMF. A comparison of these results with those obtained in the related DMF-methanol system shows a completely different behaviour for the three salts. Whereas solubility of silver bromate increases continuously up to $X_{\text{DMF}} = 0.9$ and then shows slight decrease in the pure solvent, an exactly opposite variation is observed (Giridhar and Kalidas 1983) for silver acetate in DMF-methanol mixtures. In silver sulphate solubility passes (Stroka and Schneider 1980) through a maximum at $X_{\text{DMF}} = 0.6$ and then decreases. In acetonitrile-water mixtures where the solvent-solvent interactions are weak and the system shows positive deviation from Raoult's law (Vierk 1950), solubility of silver sulphate, silver bromate and silver acetate passes through a maximum on the addition of acetonitrile and then decreases. The transfer-free energy of all the three salts continuously increases with the addition of DMF in water-DMF mixtures. The transfer-free energy of the silver ion, is, however negative and continuously decreases down to $X_{\text{DMF}} = 0.9$ and then shows a slight increase in p DMF, with the sign remaining unaffected. A similar observation is noted for the variation of the free energy of transfer of silver ion from methanol to methanol-DMF mixtures (Giridhar and Kalidas 1983). Thus the transfer of silver ion from water to water-DMF mixtures is a favourable process indicating that the silver ion is preferentially solvated by DMF. The preferential solvation of silver ion by DMF in these mixtures can be rationalised on the basis of the specific backbonding interactions between the silver cation and the π^* orbitals of the carbonyl double bond in DMF. On the other hand, the transfer-free energies of all the anions are seen to be positive and increase continuously with the addition of DMF.

with the addition of DMF. The large ΔG_i^0 values in sulphate compared to the bromate and acetate reflect the stronger ion-solvent interactions of this doubly-charged ion with water compared to that of singly-charged ions. Thus the transfer of anions from water to water-DMF mixtures is not favoured and points to a preferential hydration of the anions by water. This may be attributed to the strong H-bonding interactions between the anions and water molecules. A comparison of the transfer-free energies of the silver ion and the anions on the nLJP and reference electrolyte method (tables 1–3) shows that silver ion is more strongly solvated by DMF and the anions by water with respect to reference electrolyte method.

If, however, the transfer-free energies of the ions on the basis of ferrocene reference method are considered (Barraqué *et al* 1968), an even stronger solvation of cations by DMF and anions by water may be inferred. Thus a heteroselective solvation of the salts in these mixtures is indicated irrespective of whatever extra thermodynamic assumption is used for comparing the transfer energies of single ions.

The solvent transport number, Δ of DMF in these mixtures was calculated from the EMF data on the cell (1) using the expression,

$$E = - (RT/F) [(X''_{\text{DMF}} - X'_{\text{DMF}})/X_{\text{DMF}}(1 - X_{\text{DMF}})] \cdot \Delta \cdot (1 + \partial \ln f_{\text{DMF}}/\partial \ln X_{\text{DMF}}), \quad (6)$$

where the various terms have their usual significance (Janardhanan and Kalidas 1982). The last term in (6) represents the variation of the rational activity coefficient of DMF with solvent composition. Since the water-DMF system behaves ideally at 90°C (Ivanova and Geller 1961) and since no vapour pressure data for this system are available in literature it has been tacitly assumed that no significant departures from ideality arise for this system at 30°C and hence the activity coefficient term has been taken to be zero at all compositions in these mixtures. The EMF data of cell (1) and the calculated Δ values of DMF for the three salts are given in table 4. It is seen that the Δ values for all the three salts are positive throughout and pass through a maximum ($\Delta_{\text{max}} = 3$ at $X_{\text{DMF}} \approx 0.55$) for silver sulphate, ($\Delta_{\text{max}} = 2.5$ at $X_{\text{DMF}} \approx 0.35$) for silver bromate ($\Delta_{\text{max}} = 2.1$ at $X_{\text{DMF}} \approx 0.55$) for silver acetate respectively. Δ is given by

$$\Delta = [(X_w n_D^+ - X_D \cdot n_w^+)t_+ - (X_w n_D^- - X_D n_w^-)t_-], \quad (7)$$

Table 4. EMF data and solvent transference number, Δ of DMF for AgBrO_3 , AgOAc and Ag_2SO_4 in water-DMF mixtures at 30°C.

X_{DMF}	AgBrO_3		AgOAc		Ag_2SO_4	
	$-E^*$ (mV)	Δ	$-E^*$ (mV)	Δ	$-E^*$ (mV)	Δ
0.15	2.5	0.1	10.4	0.5	4.1	0.2
0.25	7.8	0.6	8.3	0.6	10.3	0.7
0.35	28.5	2.5	9.5	0.8	13.5	1.1
0.45	25.5	2.4	10.8	1.0	23.8	2.3
0.55	7.8	0.8	22.3	2.1	32.0	3.0
0.65	7.3	0.7	16.5	1.4	14.0	1.2
0.75	5.6	0.4	13.8	1.0	9.3	0.7
0.85	4.2	0.2	6.2	0.3	9.6	0.5
0.95	2.2	0.0	2.6	0.1	4.0	0.1

* Accurate up to ± 1 mV.

where X refers to the molefractions, n the solvation numbers of water (W) and DMF (D) and t the Hittorf transport numbers of cation and anion. In heteroselective solvation n_D^+ and n_W^- are large while the other two solvation numbers are small resulting in large positive Δ values as described earlier. Thus there is an increase of 3, 2.5 and 2.1 moles of DMF for silver sulphate, silver bromate and silver acetate respectively per Faraday relative to the mean molar velocity of solvent mixture as reference in the cathode compartment when solutions of these salts are electrolysed in water-DMF mixtures at the given composition. The enrichment of DMF in the cathode compartment arises largely through its transport by the silver ion while the anion transports water in the opposite direction, i.e. towards anode. These two effects add together and thus a heteroselective solvation results in large Δ values. These results support the conclusion based on the transfer energy variation of the ions obtained earlier.

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A new spacing law for Liesegang rings

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Abstract. The spacing laws of Jablczynski and Mathur are applied to the Liesegang rings of cobalt(II) oxinate, silver iodide and lead chromate in agar gel. Although Jablczynski's spacing law satisfactorily explains the direct Liesegang rings, it totally fails to describe the revert Liesegang rings. Similarly though Mathur's spacing law is applicable to both revert and direct types of periodic precipitation, an appreciable deviation is observed in systems with greater interspacing. A new spacing law, applicable to both revert and direct Liesegang rings, is proposed on the basis of the preferential adsorption theory of Liesegang rings. It is experimentally verified with silver iodide and lead chromate systems.

Keywords. Spacing law; cobalt(II) oxinate; silver iodide; lead chromate; revert and direct Liesegang rings; preferential adsorption theory.

1. Introduction

When a reactant diffuses through a gel containing the other reactant that will form a sparingly soluble precipitate, under suitable experimental conditions the precipitation does not spread continuously or quasicontinuously, but separate precipitation zones evolve in the form of concentric rings. This is known as Liesegang phenomenon named after its discoverer. Many sparingly soluble compounds exhibit this phenomenon. Stern (1967) has given a bibliography of the Liesegang rings exhibited by different sparingly soluble substances.

Two types of Liesegang rings have been reported in literature (Stern 1967). They are direct and revert types. In the direct type, the spacing between successive rings increases with increase in the order of the ring from the gel boundary. Gnanam *et al* (1980), Kanniah *et al* (1981a) and Ambrose *et al* (1982) have reported the direct Liesegang rings of calcite, cobalt(II) oxinate and magnesium hydroxide respectively. In the revert type, the spacing between successive rings decreases as the order of the ring increases from the gel boundary. Mathur and Ghosh (1958), Flicker and Ross (1974) and Kanniah *et al* (1981b, 1983) have reported the revert Liesegang rings of silver chromate, lead iodide and silver iodide respectively.

In this paper the existing spacing laws of Jablczynski (1923) and Mathur (1961) are applied to the Liesegang rings of cobalt(II) oxinate, silver iodide and lead chromate in agar gel. A new spacing law applicable to both revert and direct Liesegang rings is proposed on the basis of the preferential adsorption theory. It is experimentally verified with silver iodide and lead chromate systems.

2. Experiment

2.1 Direct Liesegang rings of cobalt(II) oxinate

AnalaR oxine (1.3068 g) is dissolved in 2N acetic acid solution. To this solution is added 25 % ammonia solution drop by drop until a faint but permanent turbidity is obtained. A few drops of acetic acid are added to this solution which is just sufficient to dissolve the turbidity and produce a clear solution with pH 4.25. This oxine solution is mixed with agar-agar gel solution which is made up to 300 ml with hot distilled water. This gives 0.03 M oxine in 1 % agar. Similarly 1 % agar-agar solutions containing oxine of concentrations ranging from 0.01 to 0.06 M are prepared. These clear solutions (50 ml) are poured into corning glass tubes of 20 mm diameter and allowed to set. After 3 hr, 10 ml of cobalt(II) nitrate solutions of 1.031, 0.859, 0.687, 0.515 and 0.344 M concentrations are carefully poured into the tubes over the set gel. Within a week, sharp brown coloured disc-like precipitate rings demarcated by clear void spaces are obtained.

2.2 Revert and direct Liesegang rings of silver iodide

Agar gel of 1 % by weight is prepared by boiling agar with distilled water until all undissolved particles are removed. Potassium iodide of concentration ranging from 0.001 to 0.0065 M is mixed along with the gel. Silver nitrate solution (5 ml) of concentration ranging from 0.25 to 2 M is taken over the set gel. Since silver iodide is photosensitive, the tubes are covered with black paper. The experiments are carried out at room temperature. Revert Liesegang rings of silver iodide followed by direct type have been observed in the same tube.

2.3 Revert and direct Liesegang rings of lead chromate

Hot 1 % agar gel solution (75 ml) containing lead nitrate is poured into a corning glass tube of 20 mm diameter. The concentration of lead nitrate in the gel is kept in the range of 0.001 to 0.01 M. After 3 hr of gel setting, 10 ml of potassium chromate solution of concentration ranging from 0.25 to 2.0 M is taken over the gel. Sharp yellow-coloured rings are formed with pale yellow colloidal lead chromate in the spacing between the rings. The spacing between successive rings progressively decreases, reaches a minimum value and then gradually increases with increasing order of the ring from the gel boundary (figure 1).

The experiments are carried out at room temperature, 30°C. The positions of the rings are measured accurately with a cathetometer. The flocculation value was computed with IBM 1130 computer.

3. Discussion

3.1 Jablczynski's spacing law

Jablczynski (1923) proposed the first spacing law governing the position of the ring (x)

$$x_n = x_0 p^n, \quad (1)$$

where p is known as the spacing coefficient, x_0 is a constant and n is the order of the ring

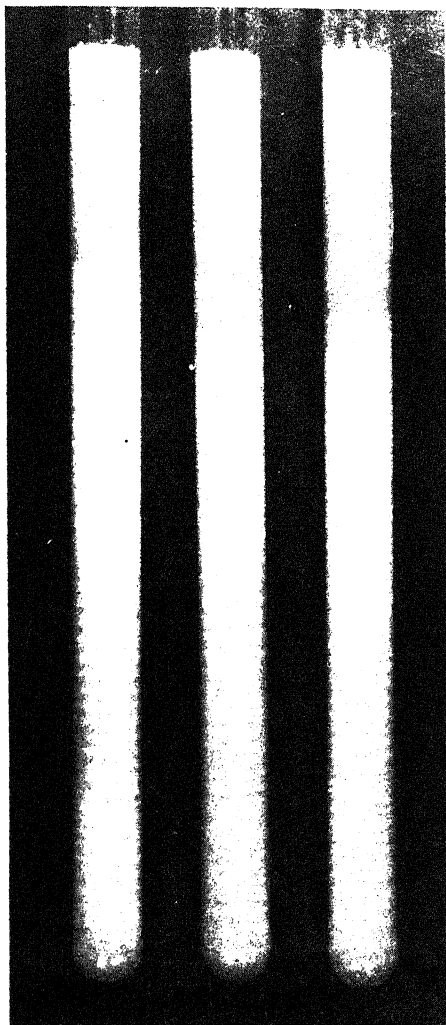


Figure 1. Revert and direct Liesegang rings of lead chromate in 1% agar gel. Concentrations of (i) potassium chromate: 2, 1.5 and 1 M (ii) lead nitrate: 0.005 M.

from the gel boundary. A plot of $\log x_n$ against n should be a straight line. This is true in many systems which exhibit the direct Liesegang phenomenon. Figure 2 represents the experimental verification of Jablczynski's spacing law with the direct Liesegang rings of cobalt(II) oxinate in agar.

Figure 3 represents the plot of $\log x$ against n for silver iodide and lead chromate systems which exhibit the revert type followed by the direct type.

It is very clear from figure 3 that the positions of rings are not governed by Jablczynski's spacing law. The rings are formed at closer and closer distances than predicted by the Jablczynski's spacing law. Although this spacing law satisfactorily explains the direct Liesegang rings, it totally fails to explain the revert type.

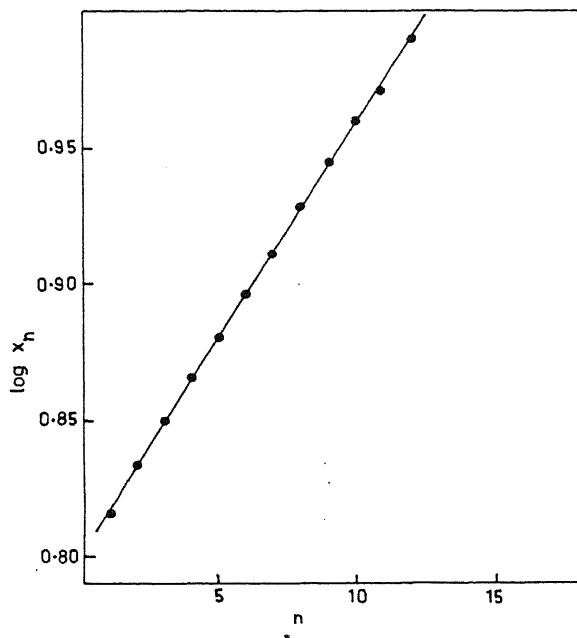


Figure 2. Experimental verification of Jablczynski's spacing law with direct Liesegang rings of cobalt(II) oxinate in agar gel.

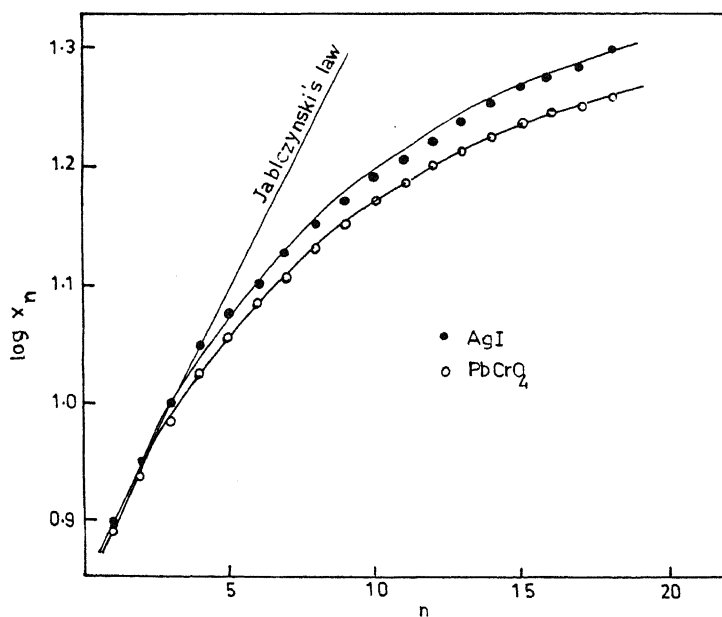


Figure 3. Deviation from Jablczynski's spacing law. Silver iodide system C_{AgNO_3} : 2 M; $C_{\text{K}_2\text{CrO}_4}$: 0.005 M. Lead chromate system $C_{\text{K}_2\text{CrO}_4}$: 1.5 M; $C_{\text{Pb}(\text{NO}_3)_2}$: 0.003 M.

3.2 Mathur's spacing law

Mathur (1961) modified Jablczynski's spacing law taking the Riemann solution to Fick's diffusion equation as given below:

$$x_n - x_{n-1} = a(S/C_0 C'_0) \exp(\alpha x_n), \quad (2)$$

where x_n and x_{n-1} represent the positions of the n th and $(n-1)$ th rings respectively from the gel boundary, S the solubility product, C_0 and C'_0 the initial concentrations of the outer and inner reactants. a and α are the characteristic constants. When α is positive, direct type rings are formed, whereas α is negative for the revert type. Mathur's spacing law can be rewritten as

$$\log(x_n - x_{n-1}) = A + \alpha x_n, \quad (3)$$

where A is a constant. The plot of $\log(x_n - x_{n-1})$ against x_n would give a straight line with positive slope for direct type and negative slope for revert type.

This spacing law has been used to determine the transition point of the revert to direct as represented in figure 4. The point of intersection represents the transition point. However a close analysis of the graph reveals an appreciable deviation from the spacing law especially for the rings with greater interspacing. This is because in the derivation of Mathur's spacing law the rings are assumed to be very close, i.e. $x_n - x_{n-1}$ is very small so that

$$\exp[\alpha(x_n - x_{n-1})] \simeq 1. \quad (4)$$

Hence an appreciable deviation from the spacing law is observed whenever the interspacing becomes considerable. In other words, this spacing law is most suitable for

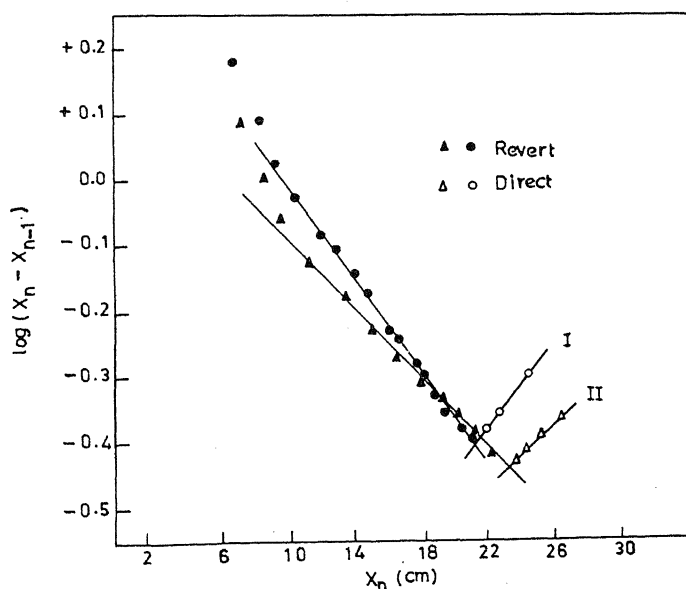


Figure 4. Deviation from Mathur's spacing law I. Silver iodide system; C_{AgNO_3} : 1.5 M; C_{KI} : 0.005 M. II. Lead chromate system, $C_{K_2CrO_4}$: 1 M; $C_{Pb(NO_3)_2}$: 0.005 M.

systems with a small number of closely-packed rings. Silver iodide and lead chromate systems contain more than 25 rings and with considerable interspacing. Hence there is an appreciable deviation from Mathur's spacing law (figure 4).

3.3 New spacing law for the revert and direct Liesegang rings

3.3a Preferential adsorption theory of silver iodide system: We have recently published (Kanniah *et al* 1983) the preferential adsorption theory of silver iodide system on the basis of the Derjaguin Landau Verwey Overbeek (DLVO) theory of the colloidal stability (Verwey and Overbeek 1928).

The concentration of silver nitrate taken over the set gel is many times greater than that of inner electrolyte, potassium iodide. When silver nitrate diffuses into the gel impregnated with potassium iodide, it first forms silver iodide particles. The preferential adsorption of excess silver ions on the surface of AgI results in the formation of positively charged silver iodide sol. Thus the silver ions peptise the silver iodide particles. The amount of the silver ions adsorbed on AgI and hence the peptising capacity are proportional to the initial concentration of the diffusing electrolyte. The surface potential of the particle (ψ_0) depends on the concentration of silver ions according to the equation

$$\psi_0 = b \log C_{Ag^+} = -b p \text{ Ag},$$

where b is a constant. As the concentration of silver ion progressively decreases from the gel boundary, the adsorption is maximum at the beginning and progressively decreases downwards. The surface potential (ψ_0) and hence the stability of the sol decrease from the gel boundary. The flocculation is effected by the counter ions which reduce the interaction potential between the sol particles to a minimum value.

According to the DLVO theory of colloidal stability (Kruyt 1952), the characteristic concentration of the outer electrolyte (Γ) to trigger the flocculation turns out to be

$$\Gamma = 8 \times 10^{-33} \psi_0^4 / A^2 Z^2 \text{ mol/l},$$

where ψ_0 is expressed in mV. As there is a concentration gradient from the gel boundary, the surface potential ψ_0 and hence the flocculation value (Γ) progressively decrease from the gel boundary leading to the formation of bands at closer and closer distances i.e., revert Liesegang rings. As the surface potential progressively decreases, a point is reached where it is equal to zero. This point is called the zero point of charge and in the present case it is the transition point of the revert Liesegang rings to direct rings.

Below the transition point the charge of AgI is reversed from positive to negative due to the release of silver ion from the AgI crystal lattice. In the crystal lattice of AgI, the more polarizable iodide ion is more strongly held than the silver ion. When the concentrations of the two ions are equal, the silver ion escapes more readily and the particle is negatively charged (Mysels 1959). As the sol is formed farther and farther away from the transition point, the silver ion escapes more and more resulting in an increase of the negative surface potential. Now the positive ions namely silver and potassium act as the counter ions which trigger the flocculation. As the negative surface potential increases, the flocculation value (Γ) progressively increases with increasing order of the ring. Hence the rings are formed farther and farther away leading to the formation of direct Liesegang rings.

Shinohara (1970) has revised the coagulation theory of Dhar and Chatterji (1968).

and derived the quantitative relation for the flocculation value (Γ) as

$$\Gamma = C_{10} \left[1 - \frac{G(f_1)}{G(f)} \right], \quad (7)$$

where

$$f_1 = f/p \text{ and } p = x_{n+1}/x_n \quad (8)$$

and

$$G(f) = \frac{1}{(2\pi)^{1/2}} \int_0^f \exp\left(-\frac{1}{2}\eta^2\right) d\eta. \quad (9)$$

If the spacing coefficient p is a constant for any two consecutive rings, then Γ is a constant. However in the silver iodide system as the spacing between successive rings progressively decreases up to the transition point and then increases gradually, Γ decreases up to the transition point and then progressively increases with increasing

Table 1. Variation of the flocculation value (Γ) with the position of the ring (x_n) in the silver iodide system (C_{AgNO_3} : 0.75 M; C_{KI} : 0.005 M).

Order of the ring n	Position of the ring x_n (cm)	Spacing coefficient $p = x_{n+1}/x_n$	Inter- spacing $x_n - x_{n-1}$ (cm)	Flocculation value Γ (mmol/l)
1	7.903	—	—	—
2	8.955	1.133	1.052	10.01
3	9.977	1.111	1.012	7.73
4	10.979	1.104	1.002	7.23
5	11.794	1.074	0.815	4.75
6	12.579	1.067	0.785	4.21
7	13.354	1.062	0.775	3.84
8	14.001	1.048	0.647	2.84
9	14.678	1.048	0.677	2.84
10	15.365	1.047	0.687	2.79
11	15.946	1.038	0.581	2.20
12	16.519	1.036	0.573	2.06
13	17.093	1.035	0.574	1.99
14	17.616	1.031	0.523	1.73
15	18.122	1.029	0.406	1.62
16	18.602	1.027	0.480	1.51
17	19.122	1.028	0.520	1.56
18	19.573	1.024	0.451	1.32
19	20.037	1.024	0.464	1.32
20	20.506	1.023	0.469	1.25
21	20.896	1.019	0.390	1.02
22	21.400	1.024	0.504	1.32
23	21.817	1.020	0.417	1.09
24	22.320	1.023	0.503	1.25
25	22.755	1.020	0.435	1.09
26	23.166	1.018	0.411	0.96
27	23.624	1.020	0.458	1.09
28	24.135	1.022	0.511	1.21
29	25.268	1.047	1.133	2.79

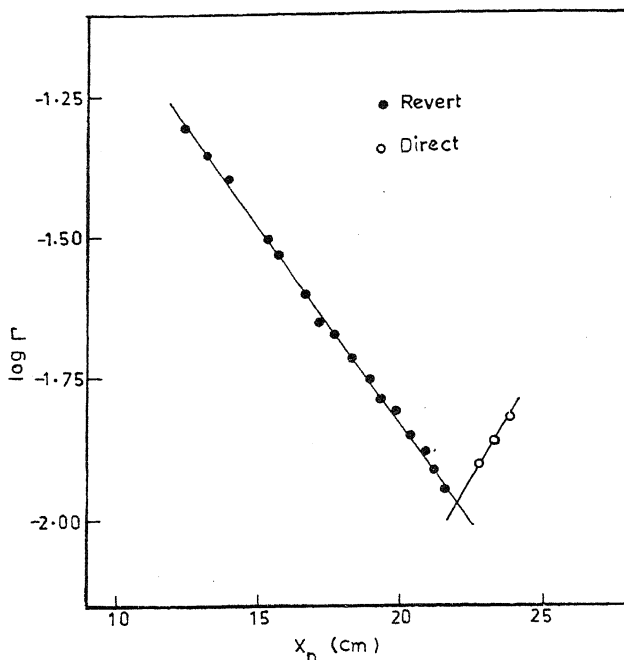


Figure 5. Experimental verification of the new spacing law with revert and direct Liesegang rings of silver iodide C_{AgNO_3} : 1.5 M C_{KI} : 0.005 M.

order of the ring from the gel boundary. Table 1 gives the variation of the flocculation value (Γ) with the order of the ring (n).

The plot of the $\log \Gamma$ against the position of the ring (x_n) gives a straight line represented in figure 5. This can be mathematically expressed as

$$\log \Gamma_n = a - b x_n, \quad (1)$$

where a and b are constants. Considering two successive rings

$$\log \Gamma_{n+1} = a - b x_{n+1} \quad (2)$$

or

$$\log \frac{\Gamma_n}{\Gamma_{n+1}} = b(x_{n+1} - x_n), \quad (3)$$

where x_{n+1} and x_n are the corresponding distances of the $(n+1)$ th and n th rings from the gel boundary and Γ_{n+1} and Γ_n are the respective concentrations of the outer electrolyte to trigger the flocculation of the sol leading to the ring formation. The spacing law (equation (12)) is applicable to both revert and direct Liesegang ring.

This spacing law is valid under different experimental conditions for obtaining revert and direct Liesegang rings of silver iodide. The best fit of the positions of the rings (figure 5) with the straight line represents the superiority of this spacing law over the existing spacing laws of Jablczynski and Mathur.

3.3.b *Lead chromate system*: When a concentrated potassium chromate solution

allowed to diffuse into the gel impregnated with lead nitrate of very low concentration, a negatively charged lead chromate sol is formed due to the preferential adsorption of excess chromate ion on lead chromate particles. Lee and Meek (1968) have established that the adsorption of chromate ion on lead chromate follows a logarithmic relation with the initial concentration of potassium chromate solution taken over the gel. Due to the adsorption of chromate ion, an electric double layer is constituted with chromate ion at the stern layer and the positively charged counter ions—potassium—predominantly at the diffuse layer. The diffuse layer also contains the negative ions due to the interpenetration of the ionic distribution.

The primary stability of the sol results from the surface charge determined by the adsorption of chromate ion. The surface potential (ψ_0) which is a measure of surface charge is related to the concentration of chromate ion as per the Lee and Meek's (1968) relation,

$$\psi_0 = a \log C_{\text{CrO}_4^{2-}} \quad (13)$$

where a is a constant. According to the DLVO theory (Kruyt 1952) the surface potential (ψ_0) is related to the flocculation value (Γ) as

$$\Gamma = 8 \times 10^{-33} \psi_0^4 / A^2 Z^2 \text{ mol/l.} \quad (6)$$

Due to the imposed concentration gradient of the diffusing electrolyte from the gel boundary the concentration of the chromate ion progressively decreases. This results in the lowering of surface potential and hence the flocculation value leading to the formation of rings at closer and closer distances up to the transition point. The zero point of charge is the point of transition from the revert to direct Liesegang rings. Due to the reversal of charge of the sol (Morimoto 1964) after the transition point, a positively-charged sol of lead chromate is formed. With increasing distance from the transition point the magnitude of the positive surface potential increases leading to an increase of flocculation value (Γ). Hence rings are formed further and further apart from each other resulting in the direct type of rings.

By suitably modifying the revised coagulation theory of Shinohara (1970), the flocculation value (Γ) at each ring has been computed (table 2). The proposed spacing law is verified with lead chromate system. The best agreement with the experimental results is well illustrated by figure 6.

4. Conclusions

Jablczynski's spacing law is valid with the direct Liesegang rings only. Mathur's spacing law explains satisfactorily the Liesegang phenomenon of a system with a smaller number of closely packed rings. The proposed spacing law satisfactorily explains both direct and revert systems.

Acknowledgement

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Table 2. The dependence of flocculation value (Γ) on the position of the ring (x_n) in the le chromate system ($C_{K_2CrO_4}$: 1 M; $C_{Pb(NO_3)_2}$: 0.003 M).

Order of the ring n	Distance of the ring (x_n) (cm)	Spacing coefficient p	Flocculation value Γ (mmol/l)
1	6.794	—	—
2	8.045	1.184	12.127
3	9.017	1.121	7.096
4	9.716	1.077	4.103
5	11.121	1.074	3.916
6	11.745	1.056	2.833
7	12.408	1.056	2.833
8	12.953	1.044	2.167
9	13.526	1.044	2.167
10	14.052	1.039	1.905
11	14.574	1.037	1.799
12	15.050	1.033	1.589
13	15.544	1.033	1.589
14	16.004	1.030	1.426
15	16.429	1.027	1.286
16	16.870	1.027	1.286
17	17.274	1.024	1.128
18	17.682	1.024	1.128
19	18.075	1.022	1.032
20	18.421	1.019	0.880
21	18.825	1.022	1.032
22	19.215	1.021	0.974
23	19.491	1.014	0.639
24	19.852	1.019	0.880
25	20.180	1.017	0.786
26	20.499	1.016	0.731
27	20.824	1.016	0.731
28	21.140	1.015	0.694
29	21.470	1.016	0.731
30	21.819	1.016	0.731
31	22.133	1.014	0.639
32	22.477	1.016	0.731
33	22.807	1.015	0.694
34	23.129	1.014	0.639
35	23.457	1.014	0.639
36	23.803	1.015	0.694
37	24.157	1.015	0.694
38	24.630	1.020	0.936
39	25.073	1.018	0.823
40	25.620	1.022	1.032

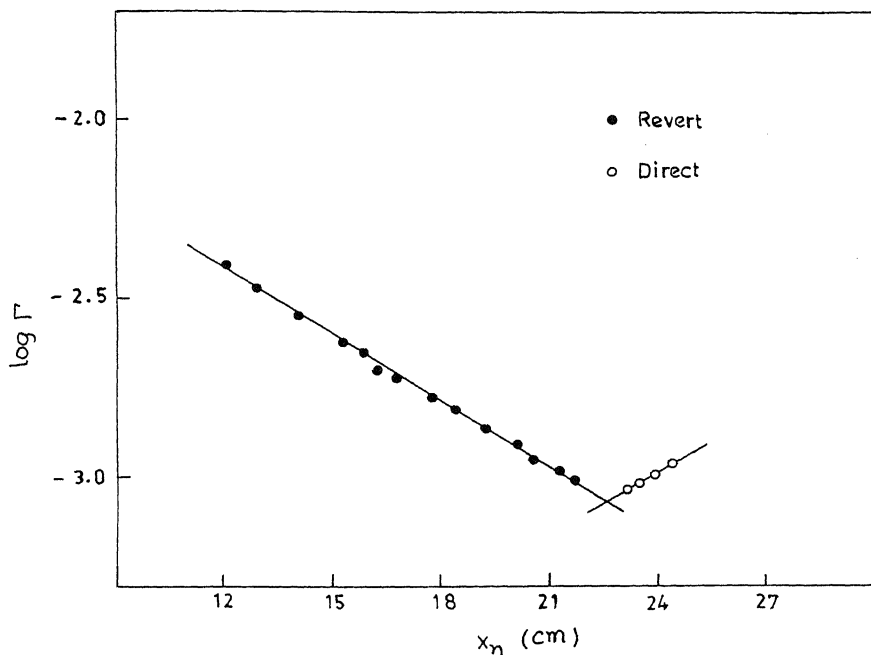


Figure 6. Experimental verification of the new spacing law with revert and direct Liesegang rings of lead chromate $C_{K_2CrO_4}$: 1 M; $C_{Pb(NO_3)_2}$: 0.005 M.

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Exchange current density as control for oscillatory reactions

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Abstract. The oscillation characteristics of the iodate systems (Briggs-Rauscher reaction) and the bromate system (Belousov-Zhabotinskii reaction) with ethylacetoacetate show that the species responsible for the oscillations in these two systems are different. This arises from a large value of the exchange current density for $\text{Pt}/\text{I}_2/\text{I}^-$. The inclusion of ferroin in an uncatalysed bromate system (UBS) leads to a switchover to a new oscillatory phase, catalysed bromate system (CBS). Oscillation in UBS is caused by a periodic change in the concentration of bromine. The switchover in oscillation characteristics on the addition of ferroin results from the value of the exchange current density for $\text{Pt}/\text{Fe(III)}/\text{Fe(II)}$ being larger than $\text{Pt}/\text{Br}_2/\text{Br}^-$.

Keywords. Oscillatory reaction; uncatalysed bromate system; exchange current density; oscillatory species; oscillatory control.

1. Introduction

The present work deals with the basic features relating to oscillatory control in the iodate and bromate systems. The range of potential, the oscillatory pattern and the static potential measurements relevant to the different systems establish that the oscillatory control in the Briggs-Rauscher (BR) and Belousov-Zhabotinskii (BZ) reactions are different.

2. Experimental

Requisite volumes of sulphuric acid, ferroin and pyrogallol were drawn from the stock solutions and kept well-stirred and thermostated in a polythene beaker. Ferroin, tris(1,10 phenanthroline) iron(II) sulphate, was prepared by mixing solutions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1,10 phenanthroline in 1:3 molar ratio. The addition of thermostated potassium bromate triggered off the oscillations. The indicator electrode (Pt and Br^- selective) was coupled to a saturated calomel electrode through a potassium nitrate salt bridge. The potential changes were continuously recorded using a $x-t$ recorder.

3. Results and discussion

Ethylacetoacetate (EAA) was employed as the substrate in the bromate and iodate systems (Savithri 1981; Ramaswamy *et al* 1982) in the presence of Mn(II) . The oscillating potential range in the bromate system is 0.9–1.1 V (vs SCE) while it is 0.5–0.7 V (vs SCE) in the iodate system. Increase in the concentration of manganese(II)

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sulphate or sulphuric acid leads to a flattening of the peak potential region in the bromate system but not in the iodate system. This could be further confirmed by the flattening of the peak region in the bromate system alone with the addition of tetra sodium pyrophosphate (Ramaswamy and Ramanathan 1983a) as the complexing agent. This could be traced to the value of the exchange current density of $\text{Pt}/\text{I}_2/\text{I}^-$ being larger (10^{-2} A/cm^2) compared to that of $\text{Pt}/\text{Mn(III)}/\text{Mn(II)}$ (10^{-5} A/cm^2) (Tanaka and Tamamushi 1964; Parsons 1959). Thus the former causes oscillations in the iodate system while in the bromate– Mn(II) system, there is a mixed control by $\text{Mn(III)}/\text{Mn(II)}$ as well as Br_2 , the exchange current density of $\text{Pt}/\text{Br}_2/\text{Br}^-$ being 10^{-5} A/cm^2 .

The uncatalysed bromate-pyrogallol system oscillates in the potential range 0.7 to 1.1 V (vs SCE) with nine oscillations in 3.5 min. Addition of ferroin has been reported to inhibit (Koros *et al* 1980) the oscillations. However the inclusion of ferroin has led to a switchover (Ramanathan and Ramaswamy 1981) to a new oscillatory phase in the region 0.95 to 1.05 V (vs SCE). Such a switchover arises because of the larger exchange current density (10^{-3} A/cm^2) for $\text{Pt}/\text{Fe(III)}/\text{Fe(II)}$ (Ramaswamy 1982) compared to that of $\text{Pt}/\text{Br}_2/\text{Br}^-$. Oscillations in Br^- in the uncatalysed bromate system could be established by employing a calibrated bromide selective indicator electrode. The concentration of Br^- at the peak and base region is about 10^{-6} M and 10^{-5} M respectively.

A direct confirmation of the fact that oscillations on a platinum electrode are caused by periodic change in the concentration of bromine is provided by the experimental simulation (Ramaswamy and Ramanathan 1983b, c) of the oscillations. Dropwise addition of bromine to a solution of acid-pyrogallol brings about a change in the potential of the platinum electrode (figure 1a). The pattern bears a striking resemblance to the self-oscillating uncatalysed bromate pyrogallol system (figure 1b). The potential variation of a platinum electrode being several times larger than the expected value can be traced to the partial misibility of the bromine-water system.

Oscillations in Br^- concentration are observed in the catalysed system as well (figure 2). The temporal behaviour of the system in Br^- is followed by a Br^- selective electrode while that of Br_2 is followed by a Pt electrode. The Pt electrode responds to changes in Br_2 and not Br^- and *vice-versa* with a Br^- selective electrode. Based on the various experimental observations, schemes of reaction for both the UBS and CBS are suggested (table 1). When Br^- concentration is large reactions (1), (2) and (3) take place and the sudden upshoot in the potential of Pt indicator electrode is seen with a corresponding decrease in Br^- (figure 2). Br^- is regenerated by steps (5) and (6) and the downtrend in the potential is due to the bromine consumption and Br^- production. Step (4) takes care of the autocatalytic production of HBrO_2 and step (7) the disproportionation of HBrO_2 . Thus the system switches back and forth between two steady states—low Br^- , high Br_2 and high Br^- , low Br_2 .

The inclusion of ferroin in the UBS modifies the scheme of reactions as indicated in steps (8) and (9). When ferroin is added reaction (8) takes place instead of (4). Fe(II) is regenerated by reaction (9) and the cycle continues.

4. Conclusion

The oscillatory pattern in any uncatalysed bromate system with a Pt electrode is due to a periodic change in the concentration of Br_2 . The inclusion of a metal ion (Mn(II)),

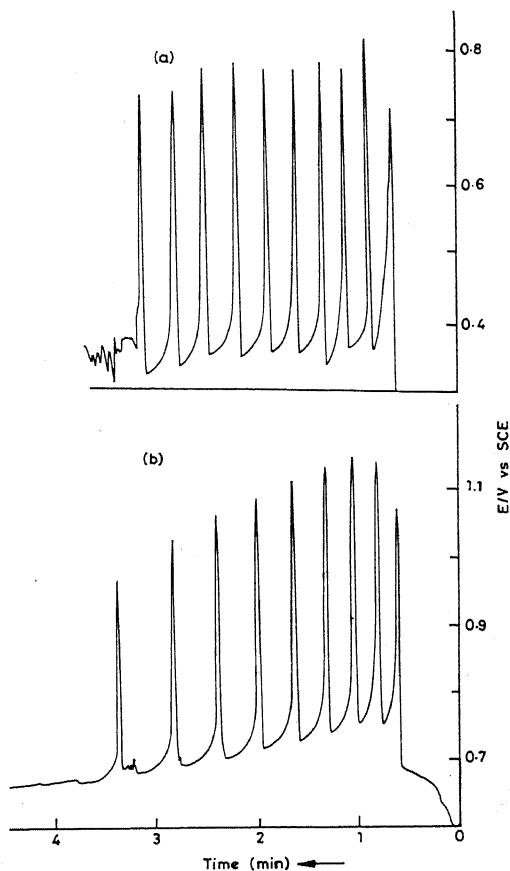


Figure 1. a. Simulated b. self-oscillating (UBS) concentration conditions in a. [Pyrogallol] = 8×10^{-3} M; $[\text{H}_2\text{SO}_4] = 0.8$ M; $[\text{Br}_2] = 10^{-3}$ M one drop at a time in b. [Pyrogallol] = 0.05 M; $[\text{H}_2\text{SO}_4] = 2$ M; $[\text{KBrO}_3] = 0.1$ M; temperature 35°C

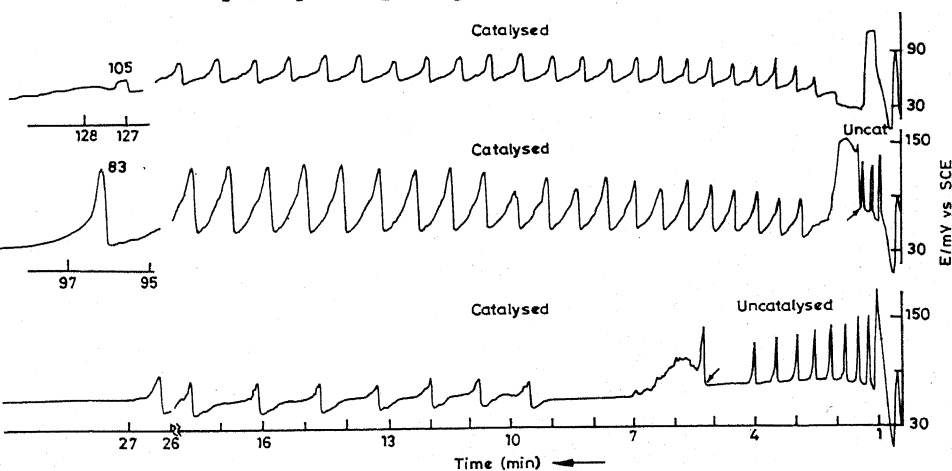


Figure 2. Oscillations in UBS and CBS with a Br^- selective electrode concentration conditions [Pyrogallol] = 0.05 M; $[\text{H}_2\text{SO}_4] = 2$ M; $[\text{KBrO}_3] = 0.1$ M; [ferriin] = 0.022 M; Temperature = 33°C → indicates the point of addition of ferriin.

Table 1. Suggested mechanism for the UBS with pyrogallol and CBS with ferroin.

	UBS
(1) $\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+$	$\rightarrow \text{HBrO}_2 + \text{HOBr}$
(2) $\text{HBrO}_2 + \text{Br}^- + \text{H}^+$	$\rightarrow 2\text{HOBr}$
(3) $\text{HOBr} + \text{Br}^- + \text{H}^+$	$\rightarrow \text{Br}_2 + \text{H}_2\text{O}$
(4) $\text{BrO}_3^- + \text{H}^+ + \text{HBrO}_2 + \text{PG}$	$\rightarrow \text{PGQ} + 2\text{HBrO}_2 + \text{H}_2\text{O}$
(5) $2\text{Br}_2 + \text{PGQ}$	$\rightarrow \text{Br}_3\text{PG} + \text{Br}^- + \text{H}^+$
(6) $\text{Br}_2 + \text{PG}$	$\rightarrow \text{BrPG} + \text{Br}^- + \text{H}^+$
(7) 2HBrO_2	$\rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+$
	CBS
(8) $2\text{Fe}^{2+} + \text{BrO}_3^- + 3\text{H}^+ + \text{HBrO}_2$	$\rightarrow 2\text{Fe}^{3+} + 2\text{HBrO}_2 + \text{H}_2\text{O}$
(9) $2\text{Fe}^{3+} + \text{Organics}$	$\rightarrow 2\text{Fe}^{2+} + 2\text{H}^+$

PG = pyrogallol; PGQ = pyrogalloquinone; BrPG = Bromopyrogallol (mono, di or tri); Br_3PG = tribromopyrogallol.

Ce(III), Fe(II)) would lead to a switchover to a new oscillatory phase if the added co has a larger value of exchange current density. The inclusion of species with compar value of exchange current density would lead to a mixed control. The oscillatory pat in any system would be that of the species possessing the largest value of excha current density at the indicator electrode.

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On thermodynamic and kinetic equivalence of chemical systems

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Abstract. A composite reaction is represented by a number of elementary reactions describing its mechanisms. By a linear transformation, the chemical flow and flux can be changed and one might obtain a new mechanism. The present report works out the selection rule to be imposed on the transformation matrix if the two mechanisms are thermodynamically and/or, kinetically indistinguishable (or equivalent). The net free energy change, entropy production, Onsager symmetry, and the detailed balance condition are considered to be the invariants of the transformation for thermodynamic equivalence. The selection rule has to be slightly modified for cyclic reactions. Two cyclic reactions with equivalent mechanisms are also worked out. It is proposed that for biochemical systems predominated by cyclic reactions, the selection rule is more permissive, and occurrence of multiple mechanisms has a higher probability, resulting in an enhancement of the fidelity of the net reaction in the presence of random environmental 'error variables'.

Keywords. Composite reaction; selection rule; transformation matrix; Onsager symmetry; entropy; thermodynamic equivalence.

1. Introduction

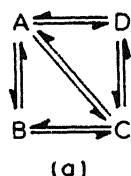
A composite reaction can generally be represented by a set of elementary reactions. Each elementary reaction has a well-defined reaction velocity given by the law of mass-action (Shear 1967). The reaction-velocity expresses a single chemical flow-vector, the corresponding affinity being the chemical driving force (Prigogine 1967; Nicolis and Prigogine 1977). Often the mechanism of a composite reaction can be described by two or more sets of flow-force descriptions each leading to the same rate of entropy production (Prigogine 1967; Meixner 1942, 1943). These systems of elementary reactions, known as equivalent systems (Prigogine 1967) are related to one another by transformation matrices (Koenig *et al* 1961). However, such transformation matrices cannot be arbitrary, since the Onsager symmetry must be retained in any transformed descriptions (Coleman and Truesdell 1960). Koenig *et al* (1961) have demonstrated that a linear transformation essentially changes the reaction mechanism without affecting the overall kinetics. It is known that so long as the reactants, products and intermediates of a given composite reaction remain unchanged, the standard free-energy change does not depend on the mechanism of the reaction. Therefore, the transformation of chemical fluxes and forces must be such that the original and the transformed system give rise to an identical change in the standard free energy.

The present report describes that the mechanism independence of standard free-energy change can serve as an additional restriction on the transformation matrix. It

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has been shown that for most composite reactions (including the reactions described by Koenig *et al* 1961), the transformation matrix reduces to an identity matrix if this invariance of standard free energy change is considered.

Looped reactions seem to have a special status in this regard. Particularly the loops which involve only isomerization reactions, are not associated with any change in the standard free energy. For such reactions, therefore, the transformation of chemical fluxes and flows seems to be more permissive. In other words, isomerization loops might involve kinetically and thermodynamically indistinguishable but mechanistically distinguishable chemical pathways. In a biological system most of the macromolecules are in states of dynamic conformational transitions. If a macromolecule can have four conformational status, say A, B, C and D, then the following two series of transitions are thermodynamically as well as kinetically indistinguishable. Now, if in mechanism (R₁a) the transition $C \rightleftharpoons A$ is affected due to any random or induced change, the thermodynamic and kinetic behaviour of the four conformers would still be unchanged. Qualitatively a multiple mechanism of a composite system increases the fidelity of the same. In contrast to looped reactions, non-cyclic chemical pathways generally lead to finite changes in standard free energy and hence the condition of invariance of free-energy-changes in indistinguishable mechanisms may be expected to be more restrictive for non-cyclic reactions than cyclic one.

(R₁)

2. Thermodynamic and kinetic indistinguishability of two reaction mechanisms

Any composite reaction C can be attributed to a particular mechanism $(M_1) = \{E_p\}$. For example, the composite reaction,



can have a mechanism expressible as



where E_1 , E_2 and E_3 are elementary reactions for which chemical affinity and reaction velocity can be explicitly defined, and X and Y are intermediates which do not appear in the overall reaction. Again, the composite reaction (R_2) can be attributed to an alternative mechanism,



which involves the same species as (M_1) .

Hence (M_1) may be transformed into $M_2 = \{E'_\rho\}$, by considering the linear transformations of macroscopic flows and forces as

$$|V'\rangle = S|V\rangle, \quad (1)$$

and,

$$|A'\rangle = T|A\rangle, \quad (2)$$

where (A, V) and (A', V') are the affinity and velocity vectors in the reference and transformed systems and S and T are the transformation matrices. Such linear transformations are called "equivalent transformations" (Prigogine 1967) provided the original and transformed systems are thermodynamically as well as kinetically equivalent.

(i) Thermodynamic indistinguishability (τ_1) of two chemical systems requires:

(a) identical rate of entropy production (E), i.e.

$$\sigma = \langle A|V\rangle = \langle A'|V'\rangle, \quad (3)$$

(b) preservation of Onsager symmetry relations (O), i.e. in near equilibrium region the linear relations,

$$|V'\rangle = L'|A'\rangle,$$

and

$$|V\rangle = L|A\rangle.$$

Satisfy

$$L' = L'', \quad (4a)$$

$$L = L'. \quad (4b)$$

(c) invariance of net change in free energy (G), which means,

$$\Delta G = \Delta G', \quad (5)$$

ΔG and $\Delta G'$ being net changes in free energy in reference and transformed systems. Since two mechanisms lead to the same overall reaction, $\Delta G_{\text{overall}}$ being independent of path, must remain invariant. Hence (5) may be thought of as an exclusion principle for transformation matrix S , such that the matrices not satisfying (G), i.e. (5), cannot describe equivalent transformation processes.

(d) invariance of solutions of detailed-balance conditions (Onsager 1931) at equilibrium (DB). Since the chemical system under consideration is assumed to be mass-closed, it would eventually reach a unique equilibrium point (Shear 1968, Gray 1970) in the limit of the ideal solution approximation (Nicolis and Prigogine 1977). Now two reaction routes will be indistinguishable if they both yield the same values of concentrations for each of the chemical species at equilibrium. Hence two sets of detailed-balance conditions must have the same set of solutions for equilibrium concentrations.

(ii) On the other hand, kinetic indistinguishability (κ_1) of two mechanisms requires the time-evolution of the concentrations of reactants to be identical in both mechanisms, i.e.

$$dC_j/dt = (dC_j/dt)', \quad (6)$$

where C_j represents the concentration of the j th chemical species ($j = 1, 2, \dots, n$, n being the total number of species involved). In fact (κ_1) does not provide any additional constraint on the transformation matrix. The validity of (E) is a sufficient condition for the validity of (κ_1) provided chemical potential vectors are conserved. Chemical

potential vector $|\mu\rangle$ being an explicit function of the activity coefficients only, remains unaltered during the transformation. We shall denote the invariance of $|\mu\rangle$ by (M) , which requires

$$|\mu\rangle = |\mu'\rangle, \quad (7)$$

where $|\mu\rangle$ and $|\mu'\rangle$ are the chemical potential vectors in the reference and the transformed systems.

3. Equivalent transformations in non-cyclic reactions

Coleman and Truesdell (1960) showed that if the transformation matrices S and T defined in (1) and (2) satisfy the relation,

$$T = (S^{-1})^t = (S^t)^{-1}, \quad (8)$$

(E) and (O) [i.e. (3) and (4)] are satisfied trivially. Such a choice, however, requires the matrix S to be non-singular. The affinity vectors can be expressed as (Nicolis and Prigogine 1977)

$$|A\rangle = -v^t|\mu\rangle, \quad (9a)$$

and,

$$|A'\rangle = -v'^t|\mu'\rangle. \quad (9b)$$

where $v = \|v_{j\rho}\|$ and $v' = \|v'_{j\rho}\|$ are stoichiometric co-efficient matrices (Boyd 1977; Prigogine 1967) in the original and transformed descriptions respectively such that $\rho = 1, 2, \dots, r$, r being the number of linearly independent simultaneous reactions. At this point, it should be mentioned that the present study deals only with those transformations which preserve the total number (r) of elementary chemical pathways in original and transformed descriptions. Since concentration evolution vector $|\dot{C}\rangle$ can be expressed as

$$|\dot{C}\rangle = v|V\rangle.$$

From (1) and (6) the condition for (K_1) is given by

$$v|V\rangle = v'|V'\rangle = v'S|V\rangle,$$

or

$$v' = v(S^{-1}). \quad (10)$$

It is now interesting to see that,

$$(i) \quad (E) \rightarrow (O). \quad (L_1)$$

Proof: (E) implies,

$$\langle A'|V'\rangle = \sigma = \langle A|V\rangle. \quad (11)$$

In near equilibrium region (Onsager 1931; Katchalsky and Curran 1967; Nicolis and Prigogine 1977), (11) yields

$$\langle A'|L'|A'\rangle = \langle A|L|A\rangle. \quad (12)$$

From (2) and (12),

$$\langle A|T^t L' T|A\rangle = \langle A|L|A\rangle,$$

or

$$\langle A|(T^t L' T) - (L)|A\rangle = 0.$$

For non-cyclic reaction A_ρ 's ($\rho = 1 \dots r$) are linearly independent. Hence

$$T'LT = L.$$

Thus in the transformation process defined by (1) and (2), L -matrix suffers a congruent transformation which retains its symmetry (Margenau and Murphy 1966; Coleman and Truesdell 1960).

Hence,

$$(L = L') \rightarrow (L' = L'').$$

Thus, (E) implies (O).

$$(ii) (E) \rightarrow (\kappa I) \quad (L_2)$$

Proof: (E) requires,

$$\langle A' | V' \rangle = \langle A | V \rangle.$$

Using (9) and (7),

$$-\langle \mu | v' | V' \rangle = -\langle \mu | v | V \rangle.$$

Since μ_j 's are linearly independent,

$$v' | V' \rangle = v | V \rangle,$$

or

$$|(\dot{C})' \rangle = |\dot{C} \rangle. \quad (13)$$

Equation (13) expresses nothing but (κI).

$$(iii) (\kappa I) \rightarrow (E) + (O) \quad (L_3)$$

Proof: Equation (11) shows that (κI) implies

$$v' = v(S^{-1}).$$

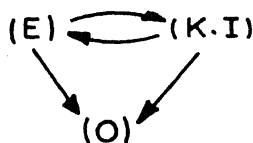
Then

$$\begin{aligned} |A' \rangle &= -v'^t |\mu' \rangle = -v'^t |\mu \rangle, \\ &= -[v(S^{-1})]^t |\mu \rangle, \\ &= -(S^{-1})^t v^t |\mu \rangle, \\ &= + (S^{-1})^t |A \rangle. \end{aligned} \quad (14)$$

Comparing equation (14) with (2), it follows that

$$T = (S^{-1})^t.$$

It has already been mentioned that the above relation [also expressed by (8)] implies the validity of both (E) and (O). Hence from the logical relations (L_1), (L_2) and (L_3), one obtains the logical triangle,



(L_4)

So far the investigators (Coleman and Truesdell 1960; Koenig *et al* 1961) considered the validity of (E), (O) and (κ_1) as sufficient criteria of thermodynamic and kinetic equivalence of two mechanisms, which may not be true, in general, since the validity of (E), (O) and (κ_1) do not ensure the validity of (G) and (DB).

Equation (5) implies nothing but the invariance of the net equilibrium constant K since

$$K_{eq} = \exp [-(\Delta G/RT)].$$

Using the law of mass-action, K_{eq} can be expressed as

$$K_{eq} = \prod_{\rho=1}^r K_{\rho} = \prod_{\rho=1}^r \prod_{j=1}^n (C_j^{eq})^{\nu_{j\rho}}, \quad (15)$$

where K_{ρ} is the equilibrium constant for ρ th elementary reaction. (κ_1) yields for a given set of initial conditions

$$(C_j^{eq}) = (C_j^{eq})', \quad (16)$$

where (C_j^{eq}) and $(C_j^{eq})'$ represents equilibrium values of C_j in the original and the transformed descriptions respectively. Then, from (5), (15) and (16), we get,

$$\sum_{j=1}^n \sum_{\rho=1}^r (\nu_{j\rho} - \nu'_{j\rho}) \ln C_j^{eq} = 0,$$

which, together with (10), yields

$$\sum_{j=1}^n \sum_{\rho=1}^r \left[\nu_{j\rho} - \sum_{\rho'=1}^r \nu_{j\rho'} (S^{-1})_{\rho'\rho} \right] \ln C_j^{eq} = 0.$$

Since C_j^{eq} depends to some extent on the initial conditions two different descriptions will yield identical changes in the net free energy irrespective of the initial conditions imposed on the system provided

$$\sum_{\rho=1}^r \sum_{\rho'=1}^r \nu_{j\rho'} [\delta_{\rho\rho'} - (S^{-1})_{\rho'\rho}] = 0. \quad (17)$$

Equation (17) provides a selection rule to the transformation matrix S for (G) to be satisfied.

At equilibrium, the forward (v_{ρ}^{+}) and reverse (v_{ρ}^{-}) velocities are equal and the detailed balance condition is given by (Gray 1970)

$$v_{\rho}^{+} = v_{\rho}^{-}$$

or,

$$k_{\rho}^{+} \prod_{j=1}^n (C_j^{eq})^{\nu_{j\rho}^{+}} = k_{\rho}^{-} \prod_{j=1}^n (C_j^{eq})^{\nu_{j\rho}^{-}}, \quad (18a)$$

where, $(v_{\rho})^{\pm}$, $k_{\rho}^{\pm}$ and $\nu_{j\rho}^{\pm}$ are reaction velocities, kinetic constants and stoichiometric coefficient of j th species in ρ th forward and backward reactions respectively in original description. Similarly, using primed notations for transformed descriptions we get the detailed-balance conditions,

$$(k_{\rho}^{+})' \prod_{j=1}^n (C_j^{eq})'^{\nu_{j\rho}^{+}} = (k_{\rho}^{-})' \prod_{j=1}^n (C_j^{eq})'^{\nu_{j\rho}^{-}} \quad (18b)$$

Equation (16) shows that (18a) and (18b) must have identical sets of solutions for C_j^{eq} . Equations (18a) and (18b) can be written in the form

$$\sum_{j=1}^n v_{j\rho} \ln C_j^{\text{eq}} = \ln \frac{k_{\rho}^{+}}{k_{\rho}^{-}} = \ln K_{\rho}, \quad (18c)$$

and

$$\sum_{j=1}^n v'_{j\rho} \ln C_j^{\text{eq}} = \ln \frac{(k_{\rho}^{+})'}{(k_{\rho}^{-})'} = \ln K'_{\rho}. \quad (18d)$$

Equation (18), together with (DB), yields

$$\sum_{j=1}^n (v_{j\rho} - v'_{j\rho}) \ln C_j^{\text{eq}} = \ln \frac{K_{\rho}}{K'_{\rho}} \quad (19)$$

where, $K_{\rho} = k_{\rho}^{+}/k_{\rho}^{-}$ and $v_{j\rho} = v_{j\rho}^{-} - v_{j\rho}^{+}$ have already been defined in (15) and (9) respectively. Equations (19) and (10), together give,

$$\sum_{j=1}^n \left[v_{j\rho} - \sum_{\rho'=1}^r v_{j\rho'} (S^{-1})_{\rho'\rho} \right] \ln C_j^{\text{eq}} = \ln \frac{K_{\rho}}{K'_{\rho}}. \quad (20)$$

Equation (20) provides another set of selection rules comprising of r number of simultaneous relations which must be satisfied by the transformation matrix S in order to satisfy (DB). Hence, two mechanisms of any composite reaction can be said to be indistinguishable, if the transformation matrix S in (1) satisfies simultaneously (3), (17) and (20), i.e. the conditions (E) [and also (O) and (κ_1)], (G) and (DB) respectively. Any transformation matrix satisfying only (E), (O) and (κ_1), may not represent indistinguishable transformations as can easily be seen from the following illustration,

$$S = \begin{pmatrix} 1 & 0 & 0 & \dots & 0 & -\alpha_1 \\ 0 & 1 & 0 & \dots & 0 & -\alpha_2 \\ 0 & 0 & 1 & \dots & 0 & -\alpha_3 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & 1 & -\alpha_{r-1} \\ 0 & 0 & 0 & \dots & 0 & 1 \end{pmatrix} \quad (21)$$

satisfying (1), (2) and (8) where $\alpha_1, \dots, \alpha_{r-1}$ are arbitrary real constants.

The transformation equations for stoichiometric coefficients in two descriptions then can be expressed as

$$v'_{j\rho} = v_{j\rho}, \quad (\rho = 1, 2, \dots, r-1).$$

$$v'_{jr} = v_{jr} + \sum_{\rho=1}^{r-1} \alpha_{\rho} v_{j\rho}.$$

The selection rule given by (G), i.e. (17) now implies

$$\sum_{\rho=1}^{r-1} \alpha_{\rho} v_{j\rho} = 0, \quad (j = 1, \dots, n) \quad (22)$$

Equation (22) represents n number of simultaneous homogeneous linear equations

(since $j = 1 \dots n$) for $(r-1)$ number of variables (α_p 's). Thus, for $r < n$, the only possible solution for (22) is $\alpha_p = 0$, for $p = 1, 2 \dots (r-1)$, i.e. $S = I$, an identity matrix.

So, for non-cyclic reactions i.e., for $r < n$, Koenig's transformation matrix (21) cannot provide two or more mechanisms which will be thermodynamically indistinguishable for arbitrary set of initial conditions. However, for a specified set of initial conditions, i.e. for a given set of equilibrium concentration, Koenig's transformation matrix given by (21) can transform a reaction mechanism thermodynamically and kinetically equivalent provided selection rule given by (17) is satisfied, i.e.,

$$\sum_{j=1}^n \sum_{p=1}^r \alpha_p v_{jp} \ln C_j^{\text{eq}} = 0. \quad (23)$$

It can be easily verified that transformation matrix S given by (21) will satisfy (23), i.e. (20), provided

$$K_p = K'_p \text{ (for } p = 1 \dots r-1), \quad (24a)$$

and

$$\sum_{j=1}^n \sum_{p=1}^{r-1} \alpha_p v_{jp} \ln C_j^{\text{eq}} = \ln \frac{K_r}{K'_r}. \quad (24b)$$

But (23) implying (G) shows that left side of (24b) vanishes, so that we can write

$$K_r = K'_r. \quad (24c)$$

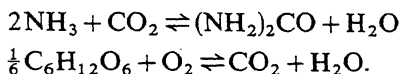
It is to be noted that even these selection rules cannot be satisfied for $r \leq 2$, since (23) takes the form

$$\alpha_1 \sum_{j=1}^n v_{j1} \ln C_j^{\text{eq}} = \alpha_1 \ln K_1 = 0, \quad (24d)$$

or

$$\alpha_1 \Delta G_1 = 0.$$

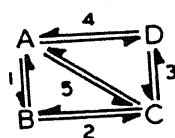
In general, the ΔG_1 , the free energy change associated with the first elementary reaction, is non-zero and has a negative sign (Keizer 1975). Thus the (24d) implies $\alpha_1 = 0$, which indicates that Koenig's transformation matrix fails to describe any other equivalent mechanism for the example cited in their work, i.e. the synthesis of urea in liver,



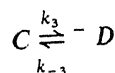
4. Example of equivalent mechanisms for monomolecular looped reactions in isolated systems

It is worth mentioning that the selection rule (17) imposed by invariance of free energy change may be trivial for looped reactions in isolated systems. To illustrate this point the reaction scheme $R_1(a)$ and (b) can be considered. As already mentioned in these schemes, A , B , C , D might be considered as four structurally interchangeable conformations of a given macromolecule (or monomolecular isomers), original

mechanism is expressed as (assuming isomerization reactions involved are elementary).



or



(R₁a)

The reaction-velocities are given by

$$|V\rangle = K|C\rangle,$$

(25)

where

$$K = \begin{pmatrix} k_1 & -k_{-1} & 0 & 0 \\ 0 & k_2 & k_{-2} & 0 \\ 0 & 0 & k_3 & k_{-3} \\ k_{-4} & 0 & 0 & k_4 \\ k_5 & 0 & k_{-5} & 0 \end{pmatrix}$$

(26)

$$|V\rangle = (V_1 \ V_2 \ V_3 \ V_4 \ V_5)^t,$$

(27a)

and

$$|C\rangle = (A \ B \ C \ D)^t.$$

(27b)

$K_{\pm\rho}$'s in (26) are kinetic constants for ρ th forward and backward reactions and A, B, C, D in (27) are the concentrations of reactants.

The affinities A_ρ 's ($\rho = 1 \dots 5$) are no longer independent since they satisfy the conservation equations

$$A_1 + A_2 + A_3 + A_4 = 0,$$

(28a)

$$A_1 + A_2 = A_5.$$

(28b)

So, choosing A_1, A_2 and A_3 as independent affinities A_1^I, A_2^I and A_3^I , we get,

$$|A^I\rangle = M|A\rangle,$$

(29)

where,

$$M = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{pmatrix}.$$

(30)

Then, the rate of entropy production σ is given by

$$\sigma = \langle A^I | V^I \rangle,$$

(31)

where,

$$|V^I\rangle = N|V\rangle,$$

(32)

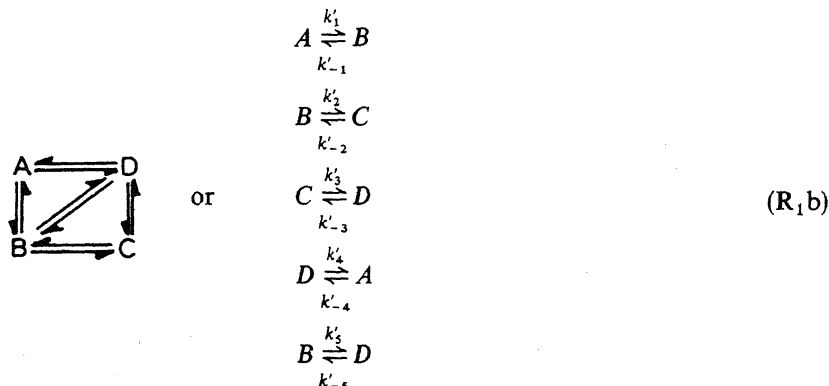
matrix N being given by

$$N = \begin{pmatrix} 1 & 0 & 0 & -1 & 1 \\ 0 & 1 & 0 & -1 & 1 \\ 0 & 0 & 1 & -1 & 0 \end{pmatrix}. \quad (33)$$

In near equilibrium region, the phenomenological velocity-affinity relation takes the form (Katchalsky and Curran 1967)

$$|V'\rangle = L|A'\rangle, \quad (34)$$

L being the symmetric Onsager matrix for mechanism $R_1(a)$. If we now consider a linear transformation of reaction rates and affinities as given by (1) and (2), where S and T are such transformation matrices that V' and A'_p represent the variable mechanism $R_1(b)$,



The rate of entropy production given by (31) and the symmetry of L -matrix in equation (34) will be preserved if transformations (1) and (2) result in linear transformations of independent flows and fluxes as

$$|(V')\rangle = R|V\rangle, \quad (35a)$$

$$|(A')\rangle = (R^T)^{-1}|A\rangle. \quad (35b)$$

where R is the transformation matrix for independent flows. For mechanism $R_1(b)$, the reaction velocity vector can be expressed as,

$$|V'\rangle = K'|C\rangle, \quad (36)$$

where

$$K' = \begin{pmatrix} k'_1 & -k'_{-1} & 0 & 0 \\ 0 & k'_2 & -k'_{-2} & 0 \\ 0 & 0 & k'_3 & k'_{-3} \\ -k'_{-4} & 0 & 0 & k'_4 \\ 0 & k'_5 & 0 & k'_{-5} \end{pmatrix} \quad (37)$$

where $k'_{\pm p}$ are kinetic constants of p th forward and backward reactions in mechanism $R_1(b)$.

At equilibrium, the detailed-balance conditions satisfied by the equilibrium concentrations A_0 , B_0 , C_0 and D_0 are given by

$$\begin{aligned} k_1 A_0 &= k_{-1} B_0; & k_2 B_0 &= k_{-2} C_0; & k_3 C_0 &= k_{-3} D_0; \\ k_4 D_0 &= k_{-4} A_0; & k_5 A_0 &= k_{-5} C_0. \end{aligned} \quad (38)$$

For mechanism R_1 (a), and,

$$\begin{aligned} k'_1 A_0 &= k'_{-1} B_0; & k'_2 B_0 &= k'_{-2} C_0; & k'_3 C_0 &= k'_{-3} D_0; \\ k'_4 D_0 &= k'_{-4} A_0; & k'_5 B_0 &= k'_{-5} D_0 \end{aligned} \quad (39)$$

for mechanism R_1 (b).

Elimination of A_0 , B_0 etc from (38) and (39) will yield

$$k'_i = (k_i/k_{-i})k'_{-i} \quad (40a)$$

for $i = 1, 2, 3$ and 4 , and,

$$k'_5 = (k_2 k_3 / k_{-2} k_{-3}) k'_{-5} \quad (40b)$$

Then, from equations (24)–(27), (37) and (40), we can write

$$k' = Uk, \quad (41)$$

where

$$U = \begin{pmatrix} k'_{-1}/k_{-1} & 0 & 0 & 0 & 0 \\ 0 & k'_{-2}/k_{-2} & 0 & 0 & 0 \\ 0 & 0 & k'_{-3}/k_{-3} & 0 & 0 \\ 0 & 0 & 0 & k'_{-4}/k_{-4} & 0 \\ 0 & (k_3/k_{-2} k_{-3})k'_{-5} & k_{-5}/k_{-3} & 0 & 0 \end{pmatrix}. \quad (42)$$

Now from equations (25)–(27), (33), (36) and (41), we get,

$$SK|C\rangle = UK|C\rangle. \quad (43)$$

Since in looped reactions all the concentrations of the reactants cannot evolve independently (43) will be satisfied for arbitrary values of C_j 's only if,

$$\det|S - U| = 0, \quad (44)$$

which, together with (42) yields

$$\det|S| = \det|U| = 0. \quad (45)$$

The transformation (34) results in a transformation in stoichiometric coefficient matrix as given by (11), i.e.

$$v'^t|\mu\rangle = Tv|\mu\rangle, \quad (46)$$

where, the stoichiometric coefficient matrices in two mechanisms R_1 (a) and R_1 (b) are respectively given by

$$v = \begin{pmatrix} -1 & 0 & 0 & +1 & -1 \\ +1 & -1 & 0 & 0 & 0 \\ 0 & +1 & -1 & 0 & +1 \\ 0 & 0 & +1 & -1 & 0 \end{pmatrix} \quad (47)$$

and,

$$v' = \begin{pmatrix} -1 & 0 & 0 & +1 & 0 \\ +1 & -1 & 0 & 0 & -1 \\ 0 & +1 & -1 & 0 & 0 \\ 0 & 0 & +1 & -1 & +1 \end{pmatrix} \quad (48)$$

so that $v_{j\rho}$ and $v'_{j\rho}$ represent stoichiometric coefficient of j th species in ρ th reaction in mechanism $R_1(a)$, $R_1(b)$ and chemical potential vector $|\mu\rangle$ being given by

$$|\mu\rangle = \begin{pmatrix} \mu_A \\ \mu_B \\ \mu_C \\ \mu_D \end{pmatrix} \quad (49)$$

in either description.

Since all the concentrations A , B , C and D are not independent, all μ_j 's no longer remain independent. Hence, (46) will be satisfied if,

$$\det |T^t(v)^t - v^t| = 0. \quad (50)$$

Transformed affinities A_ρ 's also satisfy conservation equations of the form

$$A'_1 + A'_2 + A'_3 + A'_4 = 0, \quad (51a)$$

and

$$A'_2 + A'_3 = A'_5. \quad (51b)$$

Choosing A_1 , A_2 and A_3 as independent affinities we can write,

$$|(A')\rangle = M'|A'\rangle, \quad (52)$$

where M' is of identical form as M given by (30). Similarly, independent velocities V^t will now be given by

$$|(V')\rangle = N'|V'\rangle \quad (53)$$

where,

$$N' = \begin{pmatrix} +1 & 0 & 0 & -1 & 0 \\ 0 & +1 & 0 & -1 & +1 \\ 0 & 0 & +1 & -1 & +1 \end{pmatrix} \quad (54)$$

So that rate of entropy production is given by

$$\sigma = \langle A^t | V^t \rangle \quad (55)$$

With the help of (31), (35) and (55), σ can be easily shown to be invariant.

Equations (2), (29), (35b) and (52) altogether yield

$$MT|A\rangle = (R^t)^{-1}M|A\rangle, \quad (56)$$

which will be satisfied if,

$$\det |MT - (R^t)^{-1}M| = 0. \quad (57)$$

Similarly, (1), (32) (35a) and (52) give

$$RN|V\rangle = N'S|V\rangle, \quad (58)$$

which will be satisfied provided

$$\det |RN - N'S| = 0. \quad (59)$$

Thus, the elements of (5×5) matrices S or T , and (3×3) matrix R should satisfy only four simultaneous homogeneous equations (45), (49), (57) and (59) which can always give non-trivial solutions for S_{jK} (or T_{iK}) and R_{iK} 's.

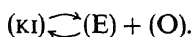
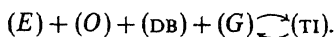
Apparently it seems that $R_1(a)$ and $R_1(b)$ cannot be kinetically equivalent since time derivative of any particular species, for example, $\dot{A}$ in $R_1(a)$ depends explicitly on C , while in $R_1(b)$, it does not. But, as long as, we are considering closed systems, the changes in concentrations are not absolutely independent and an increase in C causing changes in A , B and D , will cause equal changes in $\dot{A}$ in both $R_1(a)$ and $R_1(b)$, since $|\dot{C}\rangle$ remains invariant and the logical relation (L_2) shows that

$$\dot{A}|_{R_1(a)} = \dot{A}|_{R_1(b)}$$

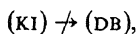
for any particular set of values for (A , B , C , D) at any given instant.

5. Discussion

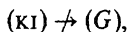
Present report emphasizes that for a given set of thermodynamic and kinetic parameters multiple indistinguishable mechanisms can exist, though the conditions of invariance of net change in free-energy and detailed-balance conditions restrict the choice of such 'equivalent' mechanisms. It is interesting to note that if two mechanisms are thermodynamically indistinguishable they will automatically be kinetically indistinguishable. However, that the reverse may not be true, is apparent from the following logical relations:



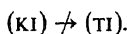
But



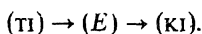
and,



Hence,



and



For cyclic reactions the role played by (G) has to be modified. In unimolecular cyclic reaction, for example, the free energy changes are zero in the original and transformed descriptions. Thus, no additional selection rule can be obtained from the invariance of net free energy change. The other logical statements are still applicable.

One of the intriguing results of the present analysis is that the existence of equivalent transformations is more restrictive for non-cyclic reactions, compared to cyclic reactions, for which the net free energy change is always zero. Hence, the probability of existence of multiple indistinguishable mechanisms is higher for cyclic relative to non-cyclic reactions. It should be emphasized here that biochemical pathways often involve closed reaction cycles, for example, any autocatalytic reaction must involve closed loop (Eigen 1971). Hence, the present observation appears significant considering that cyclic reaction besides facilitating the self-organization process, might enhance the fidelity of the system with respect to environmental perturbation.

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Calorimetric study of isomeric and steric effects amine-alcohol interactions

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Abstract. The enthalpy of complex formation between different isomers of butylamine and butylalcohol was determined at 30°C by obtaining the partial molar enthalpy of dissociation of 1:1 complexes in *n*-hexane. In both series *viz.* normal amine with isomeric alcohols and normal alcohol with isomeric amines, the enthalpy of complex formation showed the same trend as $t > n > \text{iso} > \text{sec}$.

The trend in normal-normal, normal-tertiary, tertiary-tertiary and secondary-secondary complexes was as $t-n > n-n > t-t > \text{sec}-\text{sec}$. Both these trends were explained in terms of steric and electromeric effects.

Keywords. Calorimetry; amine-alcohol interactions; isomeric effect; steric effect; enthalpy of complexes.

1. Introduction

Variation in physical properties depend on the position at which the alkyl chain is branched and the nature of the substituted group. Branching has two effects *viz* a steric effect which depends on the geometry of the substituted group and the isomeric effect (inductive + *I* or – *I* effect) which depends on the nature of the group. In the present investigation we have determined the enthalpies of complex formation between different isomers of butyl amine and butanols by dissociation method (Pradhan and Pathak 1980). The comparison of the calorimetric data thus obtained helps in understanding the effect of steric hindrance and induction on the molecular interactions between these compounds.

2. Experimental

The compounds used in the present investigation and the methods of their purification have already been given earlier (Pradhan and Mathur 1979). The heats of mixing were determined at 30°C by a calorimeter specially constructed for this purpose. The experimental details and the accuracy have been given earlier (Pradhan and Pathak 1980).

3. Results and discussion

Heats of mixing data for nine systems consisting of *n*-hexane with synthetically prepared 1:1 complexes of *n*-BuNH₂ + *n*-BuOH, *n*-BuNH₂ + iso-BuOH, *n*-BuNH₂ +

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Table 1. Heats of mixing of 1:1 complexes of isomeric butylamines and isomeric butanols with *n*-hexane at 30°C.

X_1 Mole fraction complex	ΔH (J/mol)	$\Delta H/x_1x_2$ (kJ/mol)	X_1 Mole fraction complex	ΔH (J/mol)	$\Delta H/x_1x_2$ (kJ/mol)
<i>n</i> -BuNH ₂ : <i>n</i> -BuOH					
0-0011	45	40.9	0-0040	137	34.4
0-0013	51	39.3	0-0059	187	31.9
0-0025	93	38.0	0-0087	245	28.4
0-0035	126	36.1	0-0099	262	26.7
0-0051	169	33.3	0-0123	302	24.8
0-0079	241	30.7	0-0139	325	23.7
0-0109	295	27.4	0-0216	425	20.1
0-0175	409	23.8	0-0431	628	15.2
0-0266	543	21.0	<i>n</i> -BuOH: <i>s</i> -BuNH ₂		
0-0403	673	17.4	0-0010	39	39.0
<i>n</i> -BuNH ₂ : <i>i</i> -BuOH			0-0029	103	35.6
0-0012	46	38.4	0-0062	200	32.4
0-0025	87	34.9	0-0105	278	26.7
0-0051	152	30.0	0-0150	341	23.1
0-0076	204	27.0	0-0200	386	20.7
0-0110	260	23.9	0-0258	472	18.8
0-0147	325	22.4	<i>n</i> -BuOH:1-BuNH ₂		
0-0193	395	20.9	0-0012	51	42.5
0-0322	593	17.3	0-00136	57	41.9
<i>n</i> -BuNH ₂ : <i>s</i> -BuOH			0-0036	136	38.5
0-0011	40	36.8	0-0051	188	37.0
0-0023	78	34.1	0-0058	204	35.5
0-0035	109	31.2	0-0067	223	33.5
0-0041	119	29.1	0-0081	264	32.8
0-0072	191	25.7	0-0110	314	28.9
0-0122	285	23.7	0-0216	503	23.8
0-0179	378	21.5	0-0288	587	21.0
0-0244	464	19.5	0-0378	692	19.0
0-0319	564	18.3	<i>s</i> -BuOH: <i>S</i> -BuNH ₂		
<i>n</i> -BuNH ₂ : <i>t</i> -BuOH			0-0020	68	33.9
0-00175	69	39.5	0-0036	118	32.9
0-0021	82	39.1	0-0057	179	31.6
0-00285	106	37.3	0-0084	253	30.3
0-0039	140	36.0	0-0118	339	29.1
0-0060	203	34.0	0-0141	886	27.7
0-0085	267	31.7	0-0174	449	26.3
0-0117	346	29.9	0-0220	524	24.4
0-0165	443	27.3	<i>t</i> -BuOH:1-BuNH ₂		
0-0210	520	25.3	0-00137	48.8	35.6
0-0278	620	23.0	0-0023	80	34.8
<i>n</i> -BuOH:1-BuNH ₂			0-0044	145	33.0
0-00106	41.5	39.2	0-0070	217	31.2
0-00112	44.0	39.3	0-0090	268	30.0
0-0021	80	38.1	0-0132	351	27.0
0-0021	77	36.8	0-0190	467	25.0
			0-0277	587	21.8

t-BuOH, *n*-BuNH₂ + sec. -BuOH, *n*-BuOH + iso-BuNH₂, *n*-BuOH + sec. BuNH₂, *n*-BuOH + *t*-BuNH₂, sec. BuOH + Sec. BuNH₂, *t*-BuOH + *t*-BuNH₂ are given in table 1. The $\Delta H/x_1x_2$ values have been fitted in an equation of the type

$$\Delta H/x_1x_2 = A + Bx_1 + Cx_1^2 + \dots$$

and the values of the constants are given in table 2 along with the standard deviation. The values of the enthalpy of complex formation rounded to the first decimal are given in table 3.

The enthalpy of complex formation of amines with *n*-butanol and that of butanols with *n*-butylamine shows a similar trend which is tertiary > normal > iso- > sec. In both alcohol and amine the tertiary molecule has the lowest enthalpy of self-association among the four isomers. Whereas the enthalpy of complex formation between the tertiary amine and *n*-butanol or tertiary butanol and *n*-butyl amine is higher than that between *n*-butanol and *n*-butyl amine. This reversal in the trend may be explained in terms of isomeric and steric effects.

At α -carbon atom the tertiary molecule has three methyl groups which increases the charge density on N or O atom (+ *I* effect) (Geisler *et al* 1971) and favours the hydrogen bond formation. Also the methyl groups make the molecule bulkier and introduces a steric hindrance when it interacts with other molecule.

In interaction between the tertiary and normal isomer, the steric hindrance is small as the latter does not possess the protruding methyl group. So the higher enthalpy of

Table 2. Least square constants for the equation $\Delta H/x_1x_2 = A + BX_1 + CX_1^2 \dots$

System	A	B ($\times 10^2$)	C ($\times 10^3$)	D ($\times 10^5$)	E ($\times 10^6$)	STD
<i>n</i> -BuNH ₂ : <i>n</i> -BuOH	42.66	-21.83	92.874	-19.655	15.370	0.34
<i>n</i> -BuNH ₂ : <i>i</i> -BuOH	41.91	-32.37	20.971	-65.505	75.229	0.11
<i>n</i> -BuNH ₂ : <i>s</i> -BuOH	40.71	-37.34	30.446	-11.294	14.825	0.36
<i>n</i> -BuNH ₂ : <i>t</i> -BuOH	43.06	-23.25	16.597	-66.019	97.379	0.17
<i>n</i> -BuOH: <i>i</i> -BuNH ₂	41.38	-19.28	50.122	-14.366	-71.512	0.31
<i>n</i> -BuOH: <i>s</i> -BuNH ₂	40.04	-12.75	-25.151	32.822	-63.084	0.33
<i>n</i> -BuOH: <i>t</i> -BuNH ₂	44.78	-19.76	63.824	-93.107	-38.982	0.42
<i>s</i> -BuOH: <i>s</i> -BuNH ₂	35.77	-10.63	82.767	-46.266	90.573	0.10
<i>t</i> -BuOH: <i>t</i> -BuNH ₂	36.49	-67.10	-29.059	27.339	-54.194	0.14

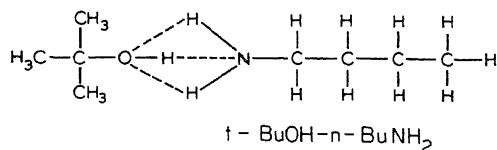
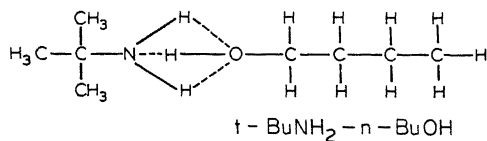
STD-Standard deviation.

Table 3. Enthalpy of complex formation of different isomeric butylamine-butyl alcohol 1:1 complexes.

Complex	$\Delta H(\pm 0.2)$ (kJ/mol)	Complex	$\Delta H(\pm 0.2)$ (kJ/mol)
<i>n</i> -BuNH ₂ : <i>n</i> -BuOH	42.7	<i>n</i> -BuOH: <i>n</i> -BuNH ₂	42.7
<i>n</i> -BuNH ₂ : <i>i</i> -BuOH	41.9	<i>n</i> -BuOH: <i>i</i> -BuNH ₂	41.4
<i>n</i> -BuNH ₂ : <i>s</i> -BuOH	40.7	<i>n</i> -BuOH: <i>s</i> -BuNH ₂	40.0
<i>n</i> -BuNH ₂ : <i>t</i> -BuOH	43.1	<i>n</i> -BuOH: <i>t</i> -BuNH ₂	44.8
<i>s</i> -BuNH ₂ : <i>s</i> -BuOH	35.8	<i>t</i> -BuOH: <i>t</i> -BuNH ₂	36.5

complex formation may be attributed to the fact that the contribution of the electromeric effect is more than the steric effect.

The enthalpy of complex formation between *t*-BuNH₂-*n*-BuOH (−44.8 kJ/mol) is about 1.7 kJ/mol more than that between *t*-BuOH-*n*-BuNH₂ (−43.1 kJ/mol). The probable reason for this may be found in the light of the model for amine-alcohol complex suggested by Huyskens *et al* (1960, 1963). The structures of *t*-BuNH₂-*n*-BuOH and *t*-BuOH-*n*-BuNH₂ complex are shown below (scheme 1).



In *t*-BuNH₂-*n*-BuOH complex (scheme 1) the steric repulsion between the CH₃ groups and H atoms of NH₂ group may decrease the distance between the H and oxygen atom of alcohol and favour the H bond formation. On the other hand the CH₃ group of *t*-BuOH may repel the H atoms of NH₂ away from the oxygen and weaken the H bond formation (scheme 1). So the complex formation between *t*-BuNH₂-*n*-BuOH is expected to be stronger than that between *t*-BuOH-*n*-BuNH₂.

When two tertiary molecules interact, the steric effect dominates over the isomeric effect and weakens the strength of interaction which explains the low enthalpy of self-association of tertiary butyl amine or butanol. It may be noted that the enthalpy of complex formation between the tertiary alcohol and amine (−36.5 kJ/mol) is much lower than that between the normal amine and alcohol (−42.7 kJ/mol).

In both the series; *n*-butanol-amines and *n*-butyl amine-butanols, the enthalpy of complex formation between the normal and secondary isomers is the least amongst the four isomers. In secondary butyl molecule the methyl group at α -carbon atom does not seem to make any significant electromeric contribution, probably due to the sharing of the effect between −CH₂− and functional groups. Thus the decrease in the enthalpy of complex formation may be due to the steric effect. According to this analogy it is expected that the enthalpy of complex formation between the two secondary isomers would be still smaller. It may be seen that the enthalpy of complex formation between secondary amine and alcohol (−35.8 kJ/mole) is smaller than that between the secondary and normal molecules (−40.7 kJ/mol).

4. Conclusions

From the present study the following conclusions may be drawn: Compared to the interactions between two normal isomers (i) The interactions between normal and iso-

isomers are weakened due to the steric effect of methyl group at β -carbon atom. (ii) The substitution of one methyl group at the α -carbon atom does not make significant electromeric contribution to the functional group. On the other hand due to the proximity of the CH_3 group the steric effect is more than that in the iso-isomer. (iii) In tertiary butyl molecule due to three methyl groups at the α carbon atom there is a $+I$ electromeric effect which strengthens the hydrogen bond formation. (iv) When two tertiary molecules interact, the steric hindrance outweighs the electromeric effect and the hydrogen bond becomes weaker. On the other hand when a tertiary molecule interacts with a normal isomer the steric effect is much reduced and the hydrogen bond formation is stronger due to $+I$ effect.

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Synergism in the extraction of uranium in presence of antipyrine

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Abstract. Synergism in the extraction of uranium(VI) has been studied in the presence of a mixture of antipyrine and β -diketones like benzoyltrifluoroacetone, trifluoroacetylacetone and furoyltrifluoroacetone. The nature of the extracted species has been ascertained from the variation of $\log D$ with pH and the concentrations of the extractants. The equilibrium constants for the synergistic species have been evaluated taking into account the protonation and partition coefficient of antipyrine.

Keywords. Synergism; uranium; β -diketones; antipyrine.

1. Introduction

Synergism in the extraction of metals has generally been studied in the presence of β -diketones in combination with alkylphosphorus esters like TBP or TOPO and to a lesser extent, with alkylphosphoric acids (Marcus and Kertes 1969; Sekine and Hasegawa 1977). The use of other donors has been comparatively meagre. We have made a systematic study on the use of other synergists like sulfoxides and nitrogen donors in the extraction of rare earths (More and Sudersanan 1980; Sudersanan and Sundaram 1981). The present work is part of our efforts in the use of other nitrogen and oxygen donors to assess their potentialities for use as donors.

Antipyrine, a substituted pyrazolone is of considerable importance in medicine. In addition, it can be considered as a starting material for other acyl substituted pyrazolones which are attracting attention for use in extraction as β -diketones. It is therefore of interest to study the role of antipyrine as an extractant and synergist. The influence of protonation and partition coefficient of antipyrine will be of interest in understanding the role of these factors on synergism. The influence of terminal group of β -diketones has also been studied systematically to understand the correlation between the stability of the adduct and the nature of participating ligands. The results are presented in this paper.

2. Experimental

2.1 Chemicals

Antipyrine (Magenta Chemicals, Bombay; BPC quality) was used as a solution in water. Solutions of benzoyltrifluoroacetone, trifluoroacetylacetone and furoyltrifluoroacetone (K and K Labs., USA) were prepared in CCl_4 , used as a diluent. Other chemicals were of analytical grade.

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2.2 Extraction studies

Extraction experiments were carried out by equilibrating 10 ml of the aqueous phase, containing uranium, antipyrine, sodium chloride, to maintain the ionic strength at 0.5, and HCl to maintain the pH, with an equal volume of the organic phase containing the β -diketone. The two phases were equilibrated at $25 \pm 1^\circ\text{C}$ using a thermostated mechanical shaker for about 4 hr, the time being sufficient for equilibration. The phases were separated and the pH of the aqueous phase was measured using a Beckman Expandomatic SS-2 pH meter. Eight ml of the organic phase was equilibrated with an acidic solution (~ 0.4 M in HCl) containing 0.5 M sodium chloride to strip uranium into the aqueous phase. The two aqueous phases were then estimated for uranium.

2.3 Estimation of uranium

Uranium was estimated spectrophotometrically using pyridylazoresorcinol (PAR). The solution containing uranium was evaporated to dryness and was then dissolved in about 4 ml of water. One ml of 0.1 M EDTA, 1 ml of solution containing 200 μg of PAR and 2 ml of 10% (V/V) ammonia were added and the solution made up to 10 ml. The optical density was measured at 540 nm with water as blank and was corrected for absorption due to the reagents alone.

2.4 Partition coefficient of antipyrine

The partition coefficient of antipyrine (APY) was determined by equilibrating an aqueous solution of APY with an equal volume of CCl_4 and determining the concentrations in the two phases by volumetry (Garratt 1964). APY was estimated by treating with iodine dissolved in about 2 g of sodium iodide to convert it to its iodo derivative. After 20 min. when the reaction was over, excess iodine was titrated, after dissolving iodo antipyrine in chloroform or CCl_4 with sodium thiosulphate using freshly prepared starch as indicator. The partition coefficient P_{APY} , was determined to be 0.12.

2.5 Dissociation constant of APY

The dissociation constant of APY K_a , was determined to be $10^{-1.38}$ by the pH-titration technique (Irving and Rossotti 1954). The protonation constant was utilised to correct for the association of protons with APY.

3. Results and discussion

Extraction of uranium was studied in the presence of antipyrine and β -diketones with a view to investigate the effect of terminal groups of the β -diketone.

3.1 Uranium-benzoyltrifluoroacetone-APY system

The distribution ratio D was measured as a function of pH and concentrations of benzoyltrifluoroacetone, HBFA and APY. The plots of $\log D$ as a function of pH, $\log [\text{HBFA}]_0$ and $\log [\text{APY}]_{\text{tot}}$ are presented in figure 1. The first two plots resulted in straight lines having a slope of about two while the plot of $\log D$ vs $\log [\text{APY}]_{\text{tot}}$ resulted

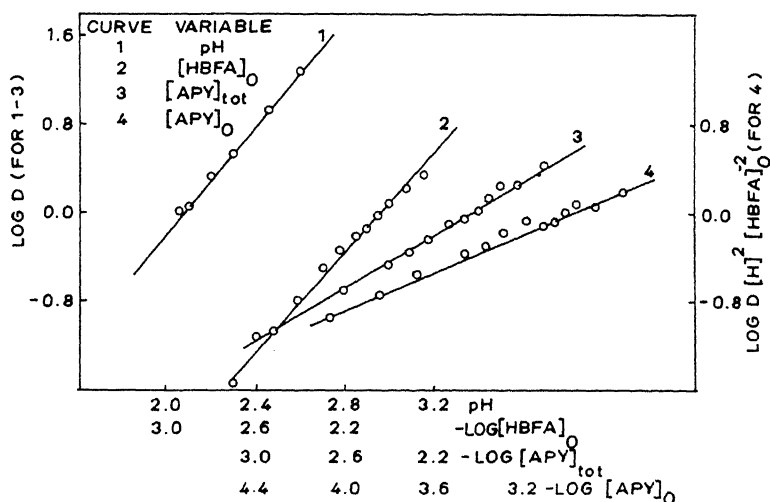


Figure 1. UO_2 -HBFA-APY- CCl_4 : log-log plots.

in a straight line with slope about one. Hence the extraction mechanism can be written as



The association of APY with protons and its partition into the organic phase were taken into account in calculating the concentration of APY in the organic phase using the relation

$$[\text{APY}]_{\text{tot}} = [\text{APY}]_0 + \frac{[\text{APY}]_0}{P_{\text{APY}}} + \frac{K_a^{-1}[\text{H}][\text{APY}]_0}{P_{\text{APY}}}. \quad (2)$$

The equilibrium constant K for the extraction reaction was calculated from

$$K = D[\text{H}]^2 [\text{HBFA}]_0^{-2} [\text{APY}]_0^{-1}. \quad (3)$$

In order to correct for the variations of pH in the measurements, $\log D [\text{H}]^2 [\text{HBFA}]_0^{-2}$ was plotted as a function of $\log [\text{APY}]_0$, which resulted in a straight line of slope 1, in agreement with the above equation. The equilibrium constant was also calculated and is presented graphically in figure 3.

3.2 Uranium-trifluoroacetylacetone-APY system

Extraction of uranium by APY was also studied in the presence of another fluorinated β -diketone, viz. trifluoroacetylacetone, HTFA. The distribution ratio was measured as a function of pH and concentrations of HTFA and APY. The concentration of APY in the organic phase was calculated, as mentioned earlier and that of HTFA was also corrected for the partition to the aqueous phase, the partition coefficient being 0.646 (Sekine *et al* 1973).

The plot of $\log D$ vs pH resulted in a straight line with a slope of 2.5 when no correction was applied for the concentration of APY in the organic phase. However, with the corrected values of $[\text{APY}]_0$, as a result of change in pH, the slope was close to two

indicating the influence of protonation on the apparent values of slope. The plot of $\log D$ vs $\log [\text{HTFA}]_0$ resulted in a slope of 2 indicating the extracted species to contain two molecules of TFA. The plot of $\log D$ vs $\log [\text{APY}]_0$ could not be made due to the change in pH and hence the variation of pH was considered (figure 2) by plotting $\log D$ vs $\log [\text{H}]^2$ vs $\log [\text{APY}]_0$. This resulted in a curve but could be approximated by a line with a slope of one corresponding to the coordination of one molecule of APY. The extraction mechanism could be written for the formation of $\text{UO}_2 (\text{TFA})_2 \text{APY}$ and the equilibrium constant was also calculated (figure 3).

The $\log K$ values however decreased, from an almost constant value, with increasing concentrations of APY, as shown in figure 3. A similar behaviour was also observed in

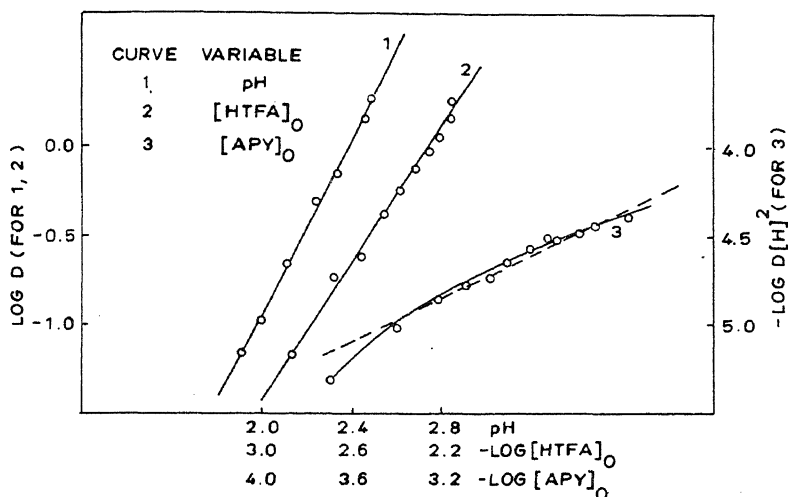


Figure 2. UO_2 -HTFA-APY- CCl_4 : log-log plots.

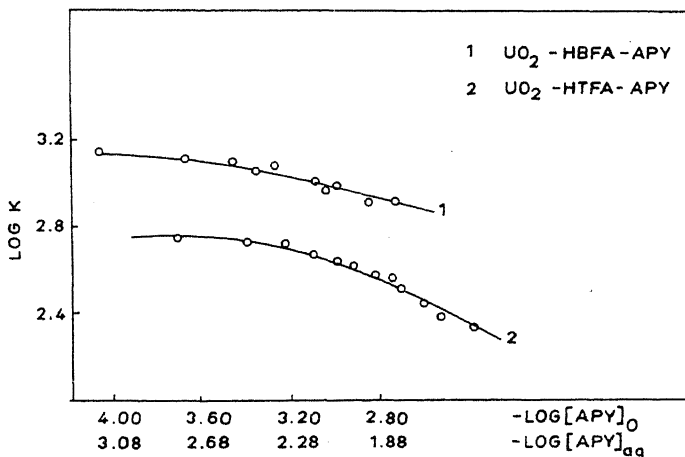


Figure 3. Variation of $\log K$ with $[\text{APY}]$.

HBFA system indicating the variation to be due to similar effects in both the cases. The decrease in the equilibrium constant may be attributed to the formation of UO_2APY complexes in the aqueous phase. The concentration of UO_2APY increases with increasing concentrations of APY, thereby causing an apparent decrease in the equilibrium constant. The data were therefore analysed by a method similar to that of aqueous phase complexes by the method of competitive reactions (Connick and Mc Vey 1949; Sudersanan and Sundaram 1976). It can be shown that

$$\frac{D_0}{D} - 1 = \left(\frac{K_0}{K} - 1 \right) = \beta'_1 [\text{APY}] + \beta'_2 [\text{APY}]^2 + \dots \quad (4)$$

where D_0 and D refer to the distribution ratios in the absence and presence of APY, K_0 and K refer to the corresponding apparent equilibrium constants and β 's refer to the stability constants of uranium APY complexes in the aqueous phase. It was found that the value of β'_1 calculated from

$$\beta'_1 = \left(\frac{K_0}{K} - 1 \right) / [\text{APY}] \quad (5)$$

was nearly constant at $10^{1.6}$ indicating the predominance of UO_2APY species. This value should however be considered only as approximate since other factors may also influence the results. The formation of uranium-antipyrine complexes was also indicated qualitatively by the appearance of a yellow colour on addition of antipyrine to uranium solutions.

3.3 Uranium-furoyltrifluoroacetone-APY systems

Extraction of uranium in the presence of APY and furoyltrifluoroacetone, HFTA, occurred at a lower pH (~ 1.8) where extraction by either HFTA or APY alone was negligible and the enhancement in extraction could be attributed to the formation of a synergistic species.

The plots of $\log D$ vs pH, $\log [\text{HFTA}]_0$ and $\log [\text{APY}]_0$, resulting in straight lines having slopes of 2.1, 2.2 and 1.2 respectively, indicated the extraction of $\text{UO}_2(\text{FTA})_2\text{APY}$. The concentration of HFTA was corrected for the transfer of the extractant to the aqueous phase using the value of 5.75 for the partition coefficient (Sudersanan and Sundaram 1978).

It was observed, in this case also, that the value of the equilibrium constant varied with the concentration of APY and hence the average $\log K$ value was taken as $10^{3.4}$. The nature of the adduct remained unchanged and only the numerical value of the equilibrium constant varied with a change in the β -diketone.

Table 1. Values of equilibrium constants for uranium- β -diketone-antipyrine adducts.

β -diketone	pK of β -diketone	$\log P_{\text{HA}}$	$\log K$
HBFA	6.01	2.47	3.15
HTFA	6.09	-0.19	2.75
HFTA	5.87	0.76	3.40

$\log P_{\text{APY}} = -0.92$; Diluent: CCl_4 .

The equilibrium constants for the various systems reported here are summarised in table 1. The effect of terminal groups of the β -diketones on synergism can be interpreted on the basis of the electron withdrawing effects of the β -diketones. In fluorinated β -diketones, the presence of electron withdrawing groups, lowers the electron density at the enol group (ring) so that the electron density at the metal is reduced. The metal ion can, therefore, form a stronger adduct with the neutral donors which are usually electron donors. The results obtained in the present case agree with the above postulates.

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Phosphate coordination in copper(II) complexes

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Abstract. The structural aspects of phosphate coordination in $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$ (1) and $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$ (2) (bipy = 2,2' bipyridyl; phen = 1,10 phenanthroline) have been investigated by IR, electronic and ESR spectra. In both complexes bidentate coordination from H_2PO_4^- ion is suggested. The complexes have been assigned *cis*-distorted octahedral stereochemistry. It is interesting that the stereochemistry is essentially of a static nature in (1) while it is fluxional in (2).

Keywords. Phosphate coordination; copper(II) phosphate complexes; spectral studies; *cis*-distorted octahedral complexes.

1. Introduction

Coordination compounds of transition metal ions containing orthophosphate ion have not been studied extensively as compared to those containing other common anions. The multivalent nature of the orthophosphate ion and its potential for multidentate coordination were expected to show an interesting variety of coordination modes. Some of the early studies reported on phosphate-coordinated complexes were on cobalt(III)-ammonia complexes containing orthophosphate and substituted orthophosphate ions (Siebert 1958; Schmidt and Taube 1963). The structural aspects of cobalt(III) and copper(II) complexes containing ammonia/other co-ligands and orthophosphate ions have been investigated by IR spectra, and both mono- and bidentate orthophosphate ions have been observed (Lincoln and Stranks 1968; Ojima and Nonoyama 1973). Studies on the hydrolytic behaviour of some of these complexes have also been reported (Lincoln and Stranks 1968).

The present work reports some of the structural aspects of phosphate ion coordination in the complexes $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$ and $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$.

2. Experimental

2.1 Chemicals

Commercially available AnalaR grade 2,2' bipyridyl, 1,10 phenanthroline, orthophosphoric acid and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were used without further purification. Ethyl alcohol was dehydrated over molecular sieve (type 5A, Union carbide) and distilled under dry nitrogen before use.

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2.2 Preparation of complexes

The complexes were prepared by reaction between $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, orthophosphoric acid and the neutral ligand in dry alcohol to minimise the water content of the medium and thereby prevent coordination of water.

2.2a $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$: Alcoholic solutions of bipy (10 mmol in 20 ml) and H_3PO_4 (10 mmol in 20 ml) were gradually added to an alcoholic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (5 mmol in 20 ml) simultaneously. The original yellowish green colour of the copper(II) chloride solution changed to green and a green precipitate (which was found to be $\text{Cu}(\text{bipy})\text{Cl}_2$) was formed in the initial stages of addition of reactants. The addition of bipy and H_3PO_4 was continued until the green colour of the supernatant solution turned pale blue. The precipitation of the green compound was complete at this stage and it was removed by filtration. To the filtrate the remaining bipy and H_3PO_4 were added when a blue compound precipitated out, which was filtered, washed and dried *in vacuo*. Yield, 0.8 g. Anal. Found: Cu, 10.6; P, 11.6; N, 8.9, H_3PO_4 , 4%; Calc. for $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$; Cu, 10.7; P, 11.7; N, 9.4; H_3PO_4 , 4.1%.

2.2b $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$. The preparation of this complex (greenish blue) is analogous to that of $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$. Yield, 0.8 g. Anal. Found: Cu, 10.0; P, 10.4; N, 9.1; H_3PO_4 , 3.5%; Calc. for $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$: Cu, 9.9; P, 10.8; N, 8.7; H_3PO_4 , 3.8%.

H_3PO_4 in the complexes was determined by the method described for solvent extraction and estimation of H_2SO_4 (Allen 1956). Both the above Cu(II) complexes were insoluble in common organic solvents. They were stable in air and melted with decomposition at 463–498 K.

2.3 Physical methods used for characterisation of complexes

IR spectra of the complexes were recorded on Perkin Elmer 577 spectrophotometer using nujol mulls. Electronic absorption spectra of nujol mulls were recorded on Cary-14 spectrophotometer. ESR spectra of powdered samples were obtained on a Varian V-4502 spectrometer operating at X-band frequencies. DPPH was used as a *g*-marker and the magnetic field was measured using an NMR gaussmeter. Magnetic susceptibilities of the compounds were measured by the Gouy method on powdered samples using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as standard.

3. Results and discussion

The electronic absorption spectrum of $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$ showed two bands due to *d-d* transitions at 13700 cm^{-1} and 10400 cm^{-1} while in $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{H}_3\text{PO}_4$ the spectrum showed a band at 12900 cm^{-1} and a shoulder at 10200 cm^{-1} (figure 1). The frequencies of the two absorption bands and the energy difference between the two transitions giving rise to these bands are closely similar to those observed for *bis*-bipy complexes of Cu(II) with *cis*-distorted octahedral stereochemistry (Hathaway *et al* 1969; Hathaway and Billing 1970; Fitzgerald *et al* 1981). This indicates that in addition to the two bidentate bipy/phen ligands the orthophosphate ion is also coordinated to the metal ion. The higher and lower energy bands observed for *cis*-distorted octahedral complexes of the type $[\text{Cu}(\text{bipy})_2\text{X}]\text{X}$ ($\text{X} = \text{NO}_2^-, \text{CH}_3\text{CO}_2^-$ etc) have been attributed to $d_{yz}, d_{xz}, d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{xy} \rightarrow d_{z^2}$

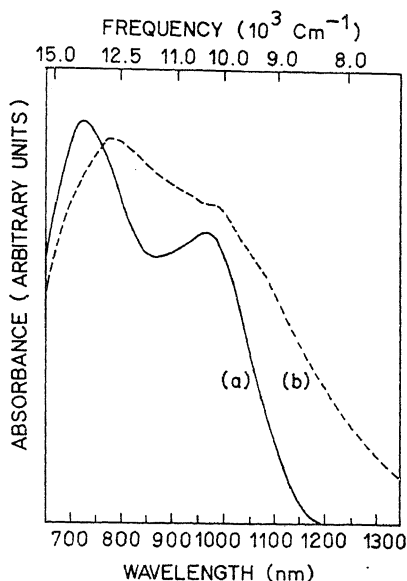


Figure 1. Electronic spectra (nujol mulls) a. $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_3\text{PO}_4$; b. $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_3\text{PO}_4$.

transitions respectively (Hathaway *et al* 1969). Therefore similar assignments may be made also in $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_3\text{PO}_4$ and $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_3\text{PO}_4$.

The IR spectra showed Cu–N stretching modes at 285 cm^{-1} (s) and 275 cm^{-1} (sh) for the copper(II)-bipy complex and at 265 cm^{-1} (sh) and 240 cm^{-1} (s) for copper(II)-phen complex as observed for tris-bipy and phen complexes of copper(II) (Saito *et al* 1972). No bands attributable to Cu–O stretching modes which are expected in the region $250\text{--}350 \text{ cm}^{-1}$ (Nuttall *et al* 1971; Contreras and Seguel 1976) were observed although electronic spectra indicated coordination of H_2PO_4^- . It is possible that Cu–O stretching modes are either obscured by the Cu–N stretching/ligand modes, or may appear only at much lower frequencies since long Cu–O bonds have been observed in related complexes (Hathaway *et al* 1969). The different P–O stretching modes formed two broad bands, at $1050\text{--}1200 \text{ cm}^{-1}$ and around 970 cm^{-1} . The in-plane bending mode characteristic of $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ was observed at 1240 cm^{-1} which showed a downward shift of $\sim 40 \text{ cm}^{-1}$ with respect to the corresponding band for H_2PO_4^- in NaH_2PO_4 (Chapman and Thirlwell 1964). This is indicative of slight weakening of the hydrogen bonds in the complexes (Chapman and Thirlwell 1964). Other bands due to H_2PO_4^- and H_3PO_4 were observed in the expected region (Chapman and Thirlwell 1964). The bipy and phen bands in the region $1050\text{--}1200 \text{ cm}^{-1}$ were found superimposed on the broad bands due to H_2PO_4^- and H_3PO_4 referred to above. The remaining bands due to bipy and phen were observed in the expected region (Inskeep 1962; Saito *et al* 1972).

The ESR spectrum of polycrystalline $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_3\text{PO}_4$ at room temperature was anisotropic with the g values 2.106 ± 0.001 ($g_{\perp}$) and 2.173 ± 0.001 ($g_{\parallel}$). At liquid nitrogen temperature the ESR spectrum contained prominent peaks with g

values 2.187 ± 0.001 (g_z), 2.109 ± 0.001 (g_y) and a shoulder with g value 2.028 ± 0.001 (g_x) suggesting a small non-axial distortion of the complex at 77° K. On the other hand the room temperature ESR spectrum of $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_2\text{PO}_4$ was isotropic with a g value of 2.125 ± 0.001 whereas at liquid nitrogen temperature the spectrum became anisotropic with g values 2.079 ± 0.001 ($g_{\perp}$) and 2.182 ± 0.001 ($g_{\parallel}$). The spectra exhibiting these features are shown in figure 2a-d. The g values observed for the copper(II)-bipy complex at 77 K ($g_z > (g_x + g_y)/2 > 2$) and copper(II)-phen complex ($g_{\parallel} > g_{\perp} > 2$) suggest *trans* octahedral structures (Hathaway and Billing 1970), but such structures are highly unlikely for *bis*-bipy and phen complexes of Cu(II) (Hathaway *et al* 1969) and other first row transition metal ions in +2 oxidation state (McKenzie 1971). This has been attributed to strong steric repulsions that may occur in such structures between the α -hydrogen atoms of the two ligand molecules. ESR spectral features similar to those for the above phosphatocomplexes of copper(II) have also been observed for *cis*-distorted octahedral *bis*-bipy and phen complexes of copper(II) containing other bidentate oxyanions (Fitzgerald *et al* 1981; Clifford *et al* 1982). These complexes have been assigned pseudo *cis*-distorted octahedral structures (I) arising from pseudodynamic Jahn-Teller effect in some cases, and square pyramidal distorted octahedral structures (II) of an essentially static nature in other cases. In addition,

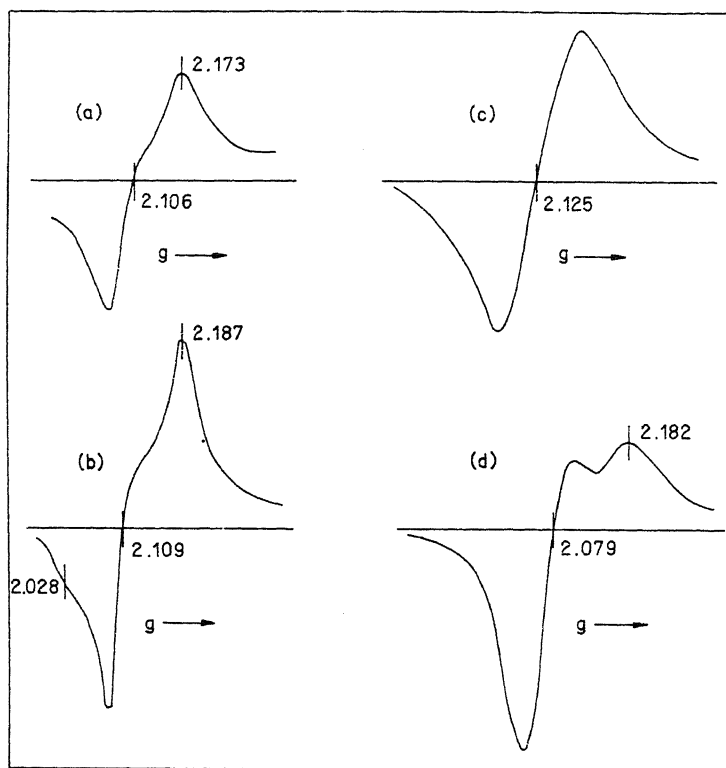


Figure 2. ESR spectra: $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_2\text{PO}_4$ at a. room temperature b. liquid nitrogen temperature; $\text{Cu}(\text{phen})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_3\text{PO}_4$ at c. room temperature d. liquid nitrogen temperature.

structures of intermediate character between (I) and (II) have also been observed. These structures show asymmetric coordination of bidentate anions like NO_2^- and CH_3COO^- with two Cu–O bonds of different bond lengths as determined by room temperature x-ray crystallography. The difference in the Cu–O bond length can be as high as 0.6 Å (structure type II) or almost negligible in some cases (structure type I). The copper(II) dihydrogen phosphate complexes of bipy and phen are also expected to have similar structures in view of the evidence from electronic and ESR spectra and are therefore formulated as $[\text{Cu}(\text{L})_2(\text{H}_2\text{PO}_4)] [\text{H}_2\text{PO}_4] \sim 0.25 \text{ H}_3\text{PO}_4$ (L = bipy or phen) in which bidentate coordination from H_2PO_4^- ion has been assumed by analogy with their counterparts containing other oxyanions (Fitzgerald *et al* 1981; Clifford *et al* 1982). The room temperature magnetic moments of the bipy and phen complexes were 1.9 B.M. and 2.08 B.M. respectively and are in the expected range (Figgis and Lewis 1960).

The ESR spectra of $\text{Cu}(\text{bipy})_2(\text{H}_2\text{PO}_4)_2 \sim 0.25 \text{ H}_3\text{PO}_4$ showed very little variation with temperature and therefore it appears to have a stereochemistry which is essentially of a static nature. However, there is a significant variation of the ESR spectra of the phen analogue with temperature which shows the fluxional nature of the CuN_4O_2 chromophore in the molecule (Fitzgerald *et al* 1981; Clifford *et al* 1982). This can arise if the magnitudes of the energy barriers separating the three available potential energy wells (each corresponding to an elongated chromophore with the elongation axes misaligned in three mutually perpendicular directions) in the bipy complex are different from those of the phen complex (Fitzgerald *et al* 1981; Clifford *et al* 1982). The structures suggested for these complexes lack axial symmetry and three g values are expected. The ESR spectra at liquid nitrogen temperature appear to show a third g value (symptomatic of a further distortion to symmetry lower than axial) only in the bipy complex. It is perhaps possible that for such a transition (averaged non-axial $\rightarrow$ static non-axial) a still lower temperature is required in the phen analogue.

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Facile chlorination of acetophenone by chloramine-T in the cationic micellar phase

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Abstract. The chlorination of acetophenone by chloramine-T (CAT) has been catalysed by added detergents, sodium laurylsulphate (NaLS) and cetyltrimethylammonium bromide (CTAB). Phenacyl chloride is the exclusive product of the reaction and the % yield of the product is greater in the cationic micellar phase indicating facile chlorination in this media (even in the absence of the mineral acid). Using Piskiewicz's treatment, the positive cooperativity for the micellar catalysed reactions has been calculated. At the cationic micellar phase of CTAB, the interaction between ammonium ion and phenyl and methylene groups probably leads to greater stabilisation than the simple hydrophobic association encountered in the micelle interior of NaLS.

Keywords. Chlorination of ketone; chloramine-T; micellar phase; mineral acid.

1. Introduction

Chlorination of reactive aromatic substrates such as cresols by chloramine-T (CAT) has been studied by several workers (Pryde and Soper 1931; Balasubramanian and Thiagarajan 1976; Higuchi and Hussain 1967). Although ketone chlorination (including acetophenone) has already been studied (Balasubramanian and Thiagarajan 1976), the present work attempts to delineate the nature of the transition state and the stabilising forces responsible for higher yield of chlorinated product, phenacyl chloride, in micellar phase.

2. Results and discussion

2.1 Rate dependence on [CAT] and [acetophenone]

The rate dependence on CAT has been determined by varying the initial concentration of CAT keeping the other parameters the same. The rate of disappearance of CAT follows first order kinetics both in the presence and absence of detergents (table 1). The reaction rate depends on [acetophenone] at lower concentrations but at higher concentrations, it becomes independent of [substrate]. In the presence of CTAB, the rate drops with increasing [acetophenone], attaining a minimum at higher concentrations. A similar decrease in rate with increasing [substrate] has been observed by Behme *et al* (1965) in the hydrolysis of methyl orthobenzoate in the presence of sodium dodecylsulphate. The decreasing rate with increasing substrate concentration most likely represents satur-

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Table 1. Rate dependence on [CAT] and [acetophenone].

$10^3[\text{CAT}]\text{M}$	$10^2[\text{Acetophenone}]\text{M}$	$10^5 k_{\text{obs}}\text{s}^{-1}$		
		<i>a</i>	<i>b</i>	<i>c</i>
1.5	4	—	5.5	—
2	4	—	5.8	—
4	4	—	5.7	—
2	0.8	—	2.3	—
2	1	—	2.8	—
2	1.5	—	4.2	—
2	2	1.97	5.5	46
2	3	2.7	5.6	42
2	4	3.7	5.8	22
2	5	4.0	5.6	21
2	7	—	—	23
2	8	—	—	21
2	10	—	5.9	—

(a) in the absence of detergents in 50% HOAc, in the absence of HClO_4 at 35°C. (b) in the presence of $[\text{NaLS}] = 8 \times 10^{-3}\text{ M}$ in 20% HOAc 80% HOAcH_2O (v/v) containing 0.2 M HClO_4 at 30°C. (c) in the presence of $[\text{CTAB}] = 8 \times 10^{-4}\text{ M}$ in 50% HOAc 50% H_2O (v/v) in the absence of HClO_4 at 35°C.

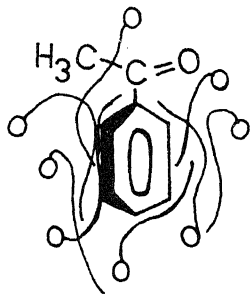
ation of the micellar phase with substrate. Thus, as substrate concentration increases beyond the saturation point, an increasing amount of the substrate must exist free in the solution. As this fraction approaches unity, the rate constant for the reaction must approach that for the reaction in purely aqueous solution and hence the observed decrease in rate.

2.2 Rate dependence on detergent concentration

Tables 2 and 3 summarise the influence of detergents, NaLS and CTAB, on the chlorination rate of acetophenone. The enhancement in rate observed is greater beyond 0.01 M NaLS, which appears to be the CMC of the detergent in the presence of reactants which is difficult to measure. This underscores the necessity of micelles in catalysing these reactions. Similar catalyses by NaLS have been observed in the chlorination of anilines (Raghavan *et al* 1980) and phenols (Rengarajan *et al* 1980) by CAT.

In the cationic micellar phase, even in the absence of mineral acid (in the absence of both mineral acid and CTAB, the rate of chlorination is very slow), the rate acceleration observed is considerable at the CTAB concentration of $4 \times 10^{-4}\text{ M}$. The reasons for the enhanced catalysis by CTAB may be manifold. The cationic micellar phase may favour enolisation considerably. Also the solubility of acetophenone in CTAB is about 2 times greater than the solubility in NaLS and the ratio of acetophenone concentration in CTAB surfactant to water varies from 19.1 to 10.5 at 23°C when the surfactant is varied from CTAB to NaLS (Fendler *et al* 1975). As the incorporation of acetophenone is greater on the hydrophobic patches (Menger *et al* 1981) where CAT and water are available, catalysis seems to be significant in CTAB than in NaLS. Also the solubilisation site of acetophenone in cationic and anionic surfactants is most likely

near the surface or in the head group region (Balasubramanian *et al* 1982), but the aromatic ring and methyl group are oriented towards the interior and the carbonyl oxygen towards the surface as shown in scheme 1 (Fendler *et al* 1975).



Scheme 1. Schematic representation of general solubilisation sites of acetophenone in aqueous micellar solution.

Table 2. Rate dependence on NaLS concentration.

$10^3 [\text{NaLS}] \text{M}$	$10^5 k_{\text{obs}} \text{sec}^{-1}$
—	5.3
4	5.4
6	5.6
10	5.5
15	5.8
20	6.2
50	7.2
60	7.8
100	9.5

[acetophenone] = 4×10^{-2} M: [CAT]
 = 2×10^{-3} M: [HClO₄] = 0.2 M: temp.
 = 30°C: solvent: 20% HOAc—80%
 H₂O.

Table 3. Rate dependence on CTAB concentration.

$10^4 [\text{CTAB}] \text{M}$	$10^5 k_{\text{obs}} \text{sec}^{-1}$
—	1.97
2	1.65
3	1.78
4	3.5
6	10
8	46
9	66
10	72

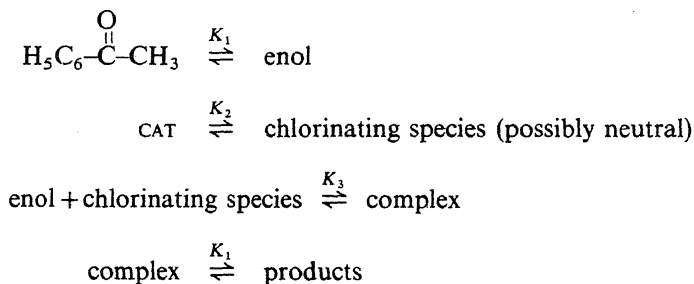
[acetophenone] = 2×10^{-2} M: [CAT]
 = 2×10^{-3} M: temp. 35°C: solvent:
 50% HOAc—50% H₂O.

As acetophenone penetrates to a greater extent in NaLS (Fendler *et al* 1975) than in CTAB, the halogenation by CAT present at the Stern layer probably becomes difficult. NMR results by Mueller (1973) confirm the progressive displacement of water from the outer core by the organic compound, affecting unequally the signals of different protons of CTAB. Along with the stabilisation of C=O group by hydrogen bonding near the surface, both phenyl and methylene groups may interact with ammonium ion distant from the surface. This may give greater stability in CTAB than the simple hydrophobic association normally encountered in the micelle interior of NaLS.

Using Piskiewicz's treatment (1977) for the micellar-catalysed reaction, the co-operativity index n calculated equals 1.11 for NaLS catalysed reaction (Raghunathan *et al* 1982) and 5.2 for the CTAB-catalysed reaction. In both cases the n value (> 1) indicates the positive co-operativity or in other words, favourable substrate-micelle interactions, a factor which seems to be responsible for the observed catalyses. This is also in keeping with the facile chlorination in the presence of cationic surfactant.

3. Mechanism of chlorination of acetophenone

The fractional order dependence observed suggests that this reaction probably proceeds *via* the intermediacy of a complex formed between substrate and CAT, exhibiting Michaelis-Menton type of kinetics. This is explained by considering the following reaction sequence:



From the reaction sequence, we derive,

$$\text{rate} = \frac{K[\text{CAT}][\text{acetophenone}]}{1 + K' \text{ acetophenone}},$$

where K and K' are the composites of K_1 , K_2 , K_3 and k_1 . At lower concentration of acetophenone, the decomposition of the complex seems to be the rate-determining step, exhibiting a fractional order dependence on acetophenone concentration. At higher concentrations, the formation of active species from CAT being the rate-determining step, a zero order dependence on acetophenone has been observed. As both, anionic and cationic micelles catalyse the reaction, the chlorinating species involved is probably neutral in nature.

4. Experimental

All the detergents used were of pure variety (BDH/Aldrich). The detergents were further purified by the procedure of Duynstee and Grunwald (1959) CAT [Societe des usines

Table 4. Stoichiometry.

[CAT]M	[Substrate]M	[CAT]:[Acetophenone]
0.01 ^a	0.002	0.0018:0.002
	0.004	0.0040:0.004
0.01 ^b	0.002	0.0020:0.002
	0.004	0.0042:0.004
0.01 ^c	0.002	0.0019:0.002
	0.004	0.0038:0.004

(a) in the absence of detergent; (b) in the presence of 0.01 M NaLS; (c) in the presence of 0.001 M CTAB.

chimiques Rhone-Boulene (Paris)] was used as such and its purity (> 99%) was ascertained by iodometric procedure. The other chemicals employed were of reagent grade and used as such after checking their physical constants.

The critical micelle concentration (CMC) of the surfactants was measured spectrophotometrically using dye as probes. The course of the reaction was followed iodometrically. The pseudo first-order rate constants were evaluated from the slopes of regression lines of $\log(b-x)$ vs time. The linear regression was analysed on a micro 2200 programmable calculator (Hindustan Computers).

4.1 Stoichiometry

The stoichiometry for the chlorination of acetophenone both in the presence and absence of detergents, was 1:1 (table 4). The stoichiometric experiments were performed with CAT in excess.

4.2 Product analysis

The products were analysed in the presence as well as absence of detergents. In both cases, phenacyl chloride has been identified as the product. The typical procedure employed to analyse the chlorinated product formed from acetophenone was as follows. Acetophenone (100 mmol, 20 ml) was mixed with CAT (50 mmol, 20 ml) in the presence of 0.5 M HClO_4 (10 ml) in 20% aqueous acetic acid. After the completion of reaction the acid was neutralised and the organic materials were ether extracted. The solvent was then distilled under vacuum and the product mixture chromatographed through a silica column. The product identified was phenacyl chloride (m.p. 56°C). The above procedure was repeated in the presence of CTAB and NaLS of different concentrations in the absence of HClO_4 . After the reaction, the detergent was precipitated by adding 0.5 M KI solution and filtered. The rest of the procedure is the same as above. Table 5 summarises the yield of phenacyl chloride in the presence and absence of detergents. The yield is greater (in the absence of HClO_4) in the cationic micellar phase (in the absence of both mineral acid and detergent, chlorination does not occur).

Acknowledgement

One of the authors (PSR) thanks CSIR for a fellowship.

Table 5. Yield of phenacyl chloride in the presence and absence of detergents.

[Detergent] M	% [Phenacyl chloride]
0	2
0.001 ^a	29
0.002 ^a	58
0.01 ^b	13.6
0.02 ^b	19.4

[CAT] = 1×10^{-3} M; [acetophenone] = 1×10^{-3} M; temp. 30°C; Solvent = 20% HOAc—80% H₂O. (a) CTAB; (b) NaLS.

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Gas phase elimination of methyl group from acetophenones within the range of 10^{-11} to 10^{-6} second

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Abstract. The field ionization of acetophenone, *p*-methyl and *p*-chloroacetophenones on a $5\text{ }\mu\text{m}$ activated wire yields an abundant peak at parent minus CH_3 group. Variations of the reaction rate as a function of the decomposition times of the elimination reaction in the range 10^{-11} – 10^{-6} sec are studied. Remarkable changes in the reaction rate according to the type of the substituent are noticed.

Keywords. Field ionization; acetophenone; reaction rate.

1. Introduction

Field ionization (FI) mass spectrometry is well suited to study the kinetics of fast unimolecular decomposition processes of organic ions in the gas phase (Beckey 1971, 1977; Van der Greef 1980; Zahran and Helal 1983; Johnstone 1972). It is possible to distinguish between fast and slow decomposition reactions in the wide range 10^{-14} to 10^{-6} sec. This is due to the extremely large potential gradient in front of the field emitter.

If a wire emitter is used, normal fragment ions are formed at the surface and near the emitter surface within a time range of 5×10^{-14} – 3×10^{-11} sec. Ions formed later in the gas phase appear as tails of strongly broadened mass lines. These ions are attributed to decompositions between 3×10^{-11} and 10^{-8} sec (fast metastable ions).

The reaction time of the decomposing ion can be calculated from the observed mass displacement (Beckey 1971, 1977). The average reaction rate constants $\bar{K}(t)$ can be evaluated as recommended by Beckey (1971, 1977) from the following equation:

$$\bar{K}(t) = I_m(t)/I_M \Delta t, \quad (1)$$

where $I_m(t)$ is the fragment ion intensity at time t , I_M is the molecular ion intensity at Δt is the time interval in which decompositions give a contribution to $I_m(t)$.

If there are no focusing lenses, fragment ions formed within 10^{-8} – 3×10^{-6} sec are called metastable ions. These ions are observed at an apparent mass number $m^* = m^2/M$, where m is the mass of the fragment ion and M is the mass of the molecular ion.

If the lens voltage is varied, a new group of metastable peaks appears which is similar in shape to the normal metastable peak group. The numbers of this group are termed "metastable plateau peaks". The apparent masses of these peaks lie between the normal metastable mass at lens voltage zero and the actual mass of the fragment ion at maximum lens voltage.

Beckey (1971, 1977) discussed in detail the method of measuring the distribution of

the average rate constant in the time range available from the fast metastable peak and the metastable plateau peaks.

According to the quasi-equilibrium theory of the mass spectra the reaction rate for a certain reaction can be expressed in a simple way:

$$K = \nu[(E - C_0)/E]^{n-1}, \quad (2)$$

where ν is the frequency factor, E is the energy absorbed, C_0 is the critical energy necessary for dissociation and n is the number of free oscillators in the molecular ion.

This simple rate equation can be used to discuss the fragmentation of organic molecules in a general sense. One would expect that greater the energy transferred during ionization *i.e.* as $((E - C_0)/E)$ increases, the faster is the decomposition of the ion. Therefore for two alternative fragmentations of an ion having similar frequency factors the rates are proportional to the activation energies.

The purpose of the present study is to determine the changes in the average rates of the elimination of methyl radical by FI of *p*-methylacetophenone, *p*-chloroacetophenone and acetophenone, in the gas phase and to learn about the substituent effect on the reaction rate. An acceptor group like Cl and a donor group like CH₃ are selected as substituents to compare their effect relative to acetophenone.

2. Experimental

A mass spectrometer (Atlas CH4) equipped with a special field ion source was used. A 5 μ m tungsten wire activated with benzonitrile (Migahed and Beckey 1971) was used as a field anode. The counter electrode was placed at a distance of 0.15 cm from the field anode. The focusing system contained a cylinder used as a retarding electrode (plateau electrode) of 1 cm length. The plateau electrode was raised to a variable voltage causing a variation in the metastable ion residence times on the plateau and consequently in the arrival time of the ions at the field-free region.

Figure 1 shows the potential distributions in the source. The effect of temperature on

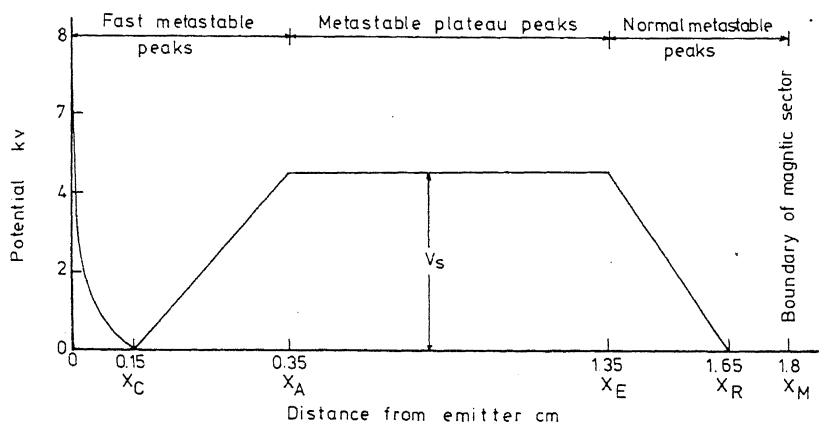
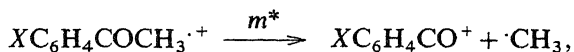


Figure 1. Potential distribution in a field ionization source with retarding electrode (X-axis: distance of electrodes from the field anode, C = counter electrode, A and E are the limits of the retarding electrode and R is the entrance slit of the first field free region).

the mass spectrum could be observed by varying the anode temperature using a direct current passing through the anode.

3. Results and discussion

The mass spectra of acetophenone, *p*-chloro and *p*-methyl acetophenones show an intense molecular ion peak which is taken as a base peak and very little fragment peaks. Elimination of CH_3 group from the molecular ions is considered as a gas phase reaction after field ionization according to the reaction:



where $X = \text{Cl}, \text{H}$ and CH_3 . This reaction is associated with the corresponding metastable peaks.

The fragment ion $(\text{M}-\text{CH}_3)^+$ is formed as a result of the C-C rupture, the bond adjacent to CO group *i.e.* it is a single bond cleavage. Helal and Zahran (1982) showed

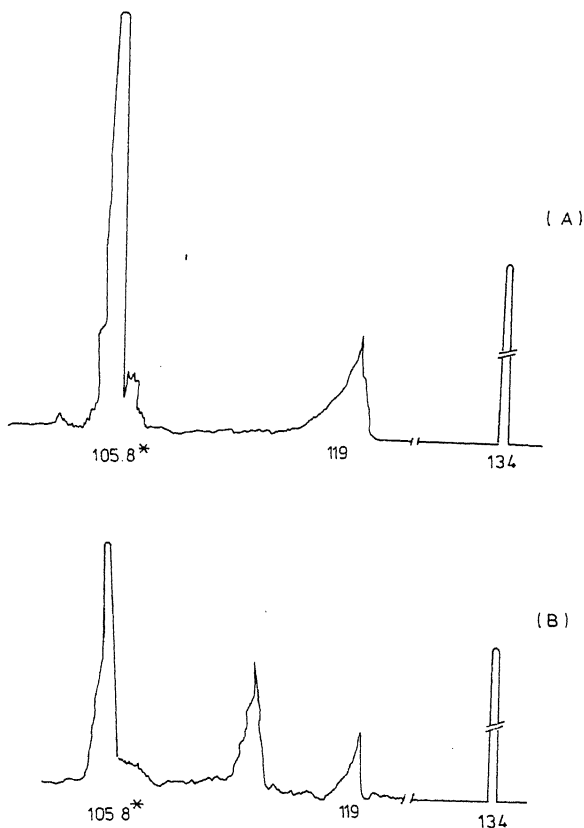


Figure 2. Part of the field ionization mass spectrum of *p*-methyl acetophenone: A-lens voltage = 0 kV, B lens voltage = 4 kV.

that the energy ΔE necessary to remove a methyl group in acetophenone from the parent ion differs from one compound to another. It is clear that the order of increase of ΔE is from *p*-chloro acetophenone to *p*-methyl acetophenone. The reaction rates may behave similar to that for the energy removal of CH_3 radical in the three molecules. The fragment ion $(\text{M}-\text{CH}_3)^+$ is formed near the emitter surface within a time range of 5×10^{-14} – 3×10^{-11} sec. Ions formed later in the gas phase and appearing as tails are attributed to decompositions between 3×10^{-11} and 10^{-8} sec, while the associated metastable ions are formed within 10^{-8} and 3×10^{-6} sec.

A new group of metastable peaks appears when the lens voltage is changed. Figure 2 shows a part of the mass spectrum of *p*-methyl acetophenone at zero lens voltage where there are no plateau peaks and at 4 kV where these peaks are of considerable intensity.

The average rate constants are measured for the elimination of the CH_3 group from acetophenone, *p*-methyl and *p*-chloroacetophenones as shown in figure 3 in the range 10^{-11} to 10^{-6} sec by the combination of the rates of the ions collected as fast metastable peaks and ions collected as plateau peaks. It is remarkable that the points originating from the two techniques fit together. This result implies the continuous distribution of the individual rate constants, which is in agreement with the statistical theory of the mass spectra.

It is clear from figure 3 that the order of increase of the average rates is from *p*-methyl acetophenone to *p*-chloroacetophenone, which is in agreement with the order of increase of energy.

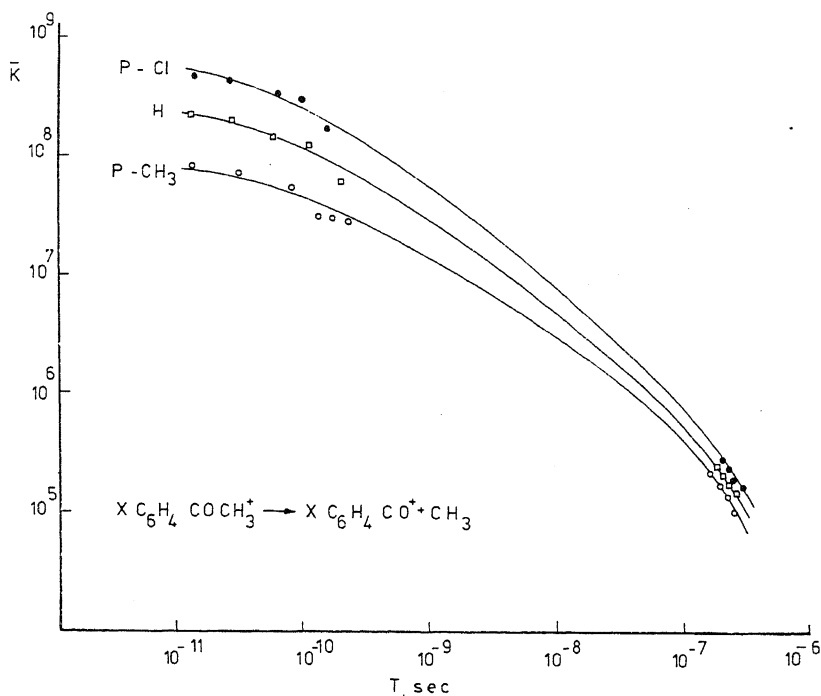


Figure 3. Average rate constants for the decomposition of acetophenone, *p*-methyl acetophenone and *p*-chloroacetophenone as a function of the ion residence time.

The dependence of the average rate constants upon the internal energy can also be obtained from the dependence of the reaction rate curves on temperature. Figure 4 shows that the relative intensity of the fragment ion $(\text{M}-\text{CH}_3)^+$ increases continuously with temperature. This can be understood according to the quasi-equilibrium theory, as the rate constant for a certain decomposition reaction is a function of the total energy transferred to the molecular ion and increase in thermal energy increases the rate of dissociation and consequently the fragment intensity.

Figure 5 shows that the curve of the average rate constant at high temperature is in general parallel to the curve obtained at room temperature but is shifted towards higher rates. This is in agreement with the statistical theory according to which the rate constants should be strongly dependent of the internal energy transferred to the molecule.

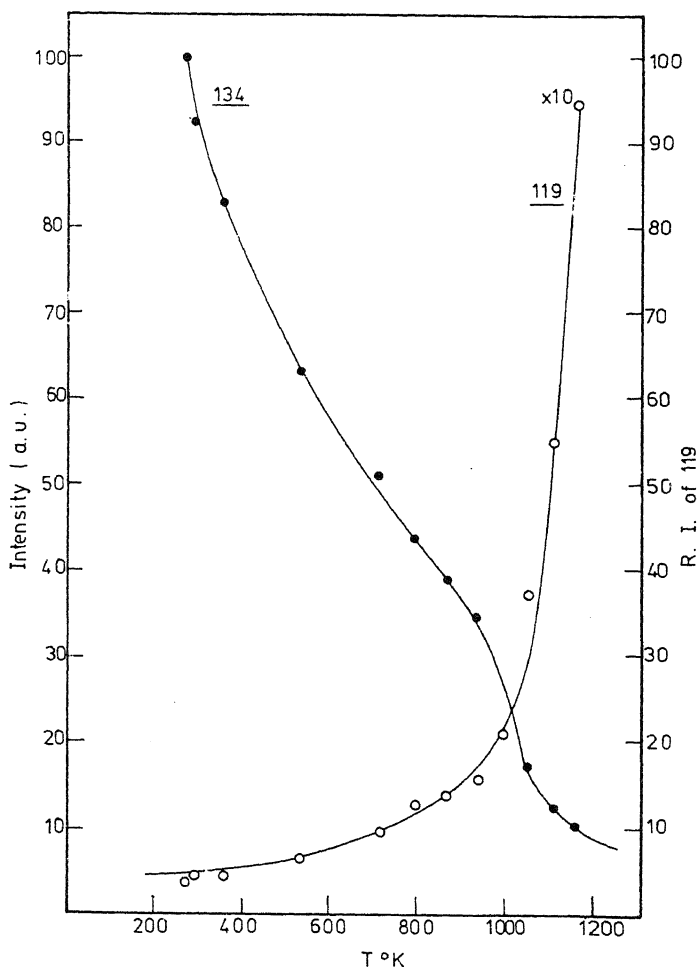


Figure 4. Variation of the ion intensities in *p*-methylacetophenone with field anode temperature (134 = parent ion and 119 = $(\text{M}-\text{CH}_3)^+$ ion).

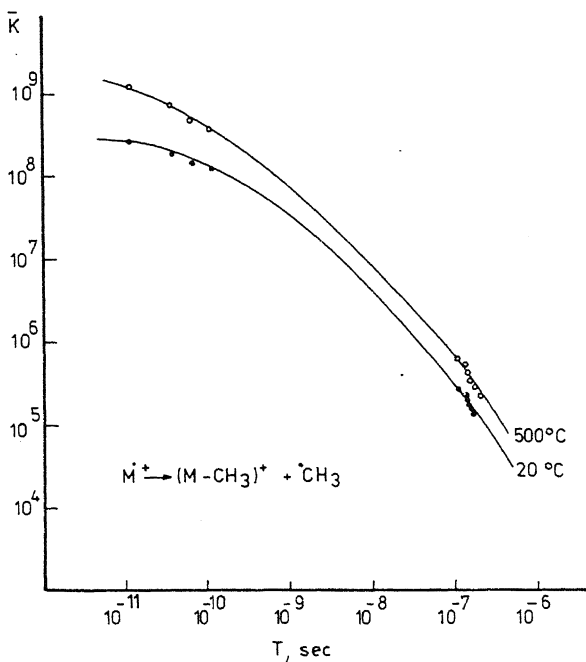


Figure 5. Average rate constants for decomposition of *p*-methyl acetophenone as a function of the ion residence time at two temperatures.

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